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May 1, 2001

Mr. Tien Q. Duong
5G-030, EE-32
Forrestal Building
U.S. Department of Energy
Washington D.C. 20585

Dear Tien:

Here is the second quarterly report for the Batteries for Advanced Transportation Technologies (BATT) Program. This report and prior (ETR) Program reports can be downloaded from <http://berc.lbl.gov/BATT/BATT.html>.

Sincerely,

Frank McLarnon
Manager
BATT Program

cc:	R. Sutula	DOE/OAAT
	K. Heitner	DOE/OAAT
	R. Kirk	DOE/OAAT
	V. Battaglia	ANL
	J. Krupa	DOE-Oakland

LBID-2358

BATTERIES FOR ADVANCED TRANSPORTATION TECHNOLOGIES (BATT)

QUARTERLY REPORT

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BATT TASK 1 CELL DEVELOPMENT

TASK STATUS REPORT

PI, INSTITUTION: K. Striebel, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Development - Cell Fabrication and Testing

SYSTEMS: Low-Cost Li-Ion, High-Power Li-Ion

BARRIER: Inconsistent evaluation of the merits of candidate novel materials.

OBJECTIVES: The primary objective is to establish a test vehicle for the evaluation of new materials for high-power and low-cost Li-ion cells.

APPROACH: The testing of novel materials in a standard cell with preset protocols will provide the necessary link between the invention of novel battery components and the diagnostic evaluation of failure modes, and will accelerate the development of a battery-powered EV. This task is a collaborative effort, which includes the development of an appropriate test vehicle (cell geometry), electrochemical cycling, and cell disassembly. Novel components will be developed in BATT Program Tasks 2, 3, and 4 (anodes, electrolytes, and cathodes) for baseline liquid and gel electrolyte chemistries. These components are incorporated into a standardized cell with appropriate ratios of components (*i.e.*, active materials/electrolyte volume) and tested with a consistent protocol to determine capacity, energy, power, and lifetime characteristics. Components are then delivered to the PI's involved with BATT Program diagnostics. Fabrication and testing of the third baseline cell, *i.e.*, Li metal/polymer/V₆O₁₃, will be carried out in the Electrolyte Task.

STATUS OCT. 1, 2000: This is a new project.

EXPECTED STATUS SEPT. 30, 2001: We expect to have semi-automated electrode preparation hardware in place. We expect to have pouch cell production hardware in place. We expect to have baseline evaluations of pouch cells (and Swagelok cells) carried out with baseline materials received from Quallion Corp. and a full testing protocol set up. We also expect to have a prototype web site set up with data from evaluation/testing of baseline cells from Doo Youn Corp. and Quallion Corp.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our milestone for the establishment of cell fabrication requires no further adjustment and should be met.

PROGRESS TOWARD MILESTONES

Accomplishments toward milestone over last quarter:

Testing of the Doo Youn pouch cells from Korea is almost complete. They were tested according to the protocol, described last quarter, at room temperature and 0°C. Higher temperature (60°C) testing was postponed until a suitable compression device could be constructed. Whereas the cells maintained more than 92% of their rated capacity after 300 cycles, the sustained (30s) peak power capability (USABC Peak Power Test) dropped by as much as 55% for the cells cycled at 25°C. While the power delivered by the cell cycled at 0°C was lower than at room temperature, as expected, the power measured after allowing this cell to warm up to room temperature was only 26% lower than the original value. This suggests that the power fade mechanism is accelerated by temperature, as noted previously within the ATD program. One cycled and two “fresh” cells were opened and delivered to the diagnostics tasks at LBNL. From their results, the cathode active material is LiCoO₂ (XRD and Raman) and the anode material appears to be a mix of MCMB-like graphite together with some more “flaky” graphite, such as SFG-6 (TEM studies).

Two other commercial cells are presently under test: a “gel” cell from Toshiba Battery Company (received courtesy of HydroQuébec) and a 100 mAh high-power cell, with the Gen 2 battery chemistry, received from Quallion Corp. The results from these cells will be summarized next quarter.

In addition to the commercial cells, we have prepared electrodes from Merck Li_{1+y}Mn_{2-y}O₄ and HydroQuébec Li₄Ti₅O₁₂ powder. These electrodes were characterized in Swagelok cells against Li metal anodes and show the expected theoretical capacity at C/25 and reasonable maintenance of that capacity up to the C-rate. This work is on-going for the verification of electrode manufacturing process. We recently received 1-side coated electrodes and 18650-size cells from Quallion Corp., all with the ATD Program Gen 2 chemistry. Performance of the Swagelok and pouch cells constructed from these electrodes will be compared with the 18650 cell performance to verify cell production techniques.

- **Further plans to meet or exceed milestones**

A preliminary web site has been deployed at <http://Battdata.lbl.gov/> for the posting of data generated in this task. Development of the database will proceed next quarter with actual test data from the BATT Program.

- **Reason for changes from original milestones:** N/A

TASK STATUS REPORT

PI, INSTITUTION: T.J. Richardson, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Development - Materials Characterization Using X-Ray Diffraction and Chemical Analysis

SYSTEMS: Li/Polymer, Low-Cost Li-Ion

BARRIER: Short lithium battery lifetimes.

OBJECTIVES: Accelerate evaluation of electrode materials by structural characterization of active components as received (or synthesized), following cell disassembly, and *in situ* during cycling. Assist in electrode materials development.

APPROACH: Analyze cycled electrodes taken from baseline BATT Program cells, seeking deleterious phase transformations in the bulk of the active material and accumulated inactive decomposition products.

STATUS OCT. 1, 2000: This is a new task.

EXPECTED STATUS SEPT. 30, 2001: Establish active material compositions of cycled and uncycled electrodes from Cell Development and Cathode investigators (Striebel and Doeff). Correlate phase transformations and accumulation of decomposition products with cell cycling performance.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Determine phase compositions in cycled electrode materials by the planned date of June 1, 2001.

PROGRESS TOWARD MILESTONES

Accomplishments toward milestone over last quarter: LiCoO₂ electrodes taken from five cycled commercial Li-ion batteries were examined by X-Ray diffraction. No new phases were found in these electrodes.

Although utilization as high as 95% of the theoretical capacity (170 mAh/g) of LiFePO₄ has been claimed¹, most researchers have achieved closer to 70% (120 mAh/g). The fluoride phosphates described below have larger pathways for Li- ion conduction and contain twice as much Li. Even with a relatively low utilization, these compounds might outperform their denser, close-packed phosphate counterparts. Li₂NiFPO₄ (Fig. 1), Na₂MnFPO₄ (Fig. 2) and Li₂CoFPO₄ (the latter previously unreported) were prepared by solid-state synthesis (Eqns. 1 and 2). Li₂CoFPO₄ was found to be isostructural with Li₂NiFPO₄.



The utility of these materials as cathodes for Li batteries is currently being assessed. Attempts to prepare the unreported compounds Li₂FeFPO₄ and Li₂MnFPO₄ by direct solid-state methods, and to prepare Li₂MnFPO₄ from Na₂MnFPO₄ by ion exchange have thus far been unsuccessful.

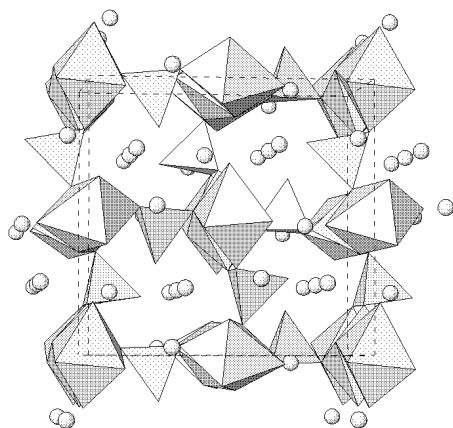


Figure 1. Li₂NiFPO₄ structure², showing NiO₄F₂ octahedra, PO₄ tetrahedra and Li ions (spheres)

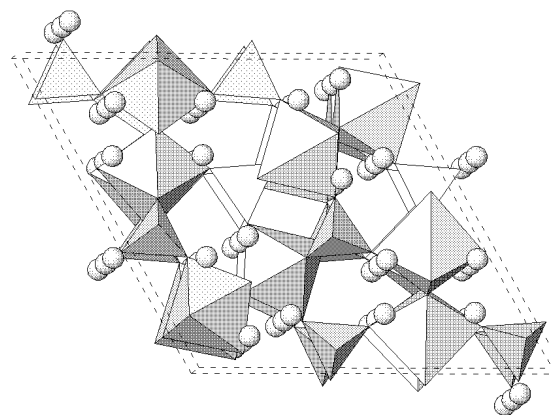


Figure 2. Na₂MnFPO₄ structure³ consisting of MnO₄F₂ octahedra, PO₄ tetrahedra and Na ions (spheres).

¹ A. Yamada, S. C. Chung, and K. Hinokuma, *J. Electrochem. Soc.*, **148**, A224 (2001).

² M. Dutreilh, C. Chevalier, M. El-Ghozzi, D. Avignant, and J. M. Montel, *J. Solid State Chem.*, **142**, 1 (1999).

³ O. V. Yakubovich, O. V. Karimova, and O. K. Mel'nikov, *Acta Cryst.*, **C53**, 395 (1997).

- **Further plans to meet or exceed milestones:** Additional potentially useful electrode materials will be synthesized and evaluated. It is anticipated that the milestone will be achieved on time.
- **Reason for changes from original milestones:** N/A

BATT TASK 2 ANODES

TASK STATUS REPORT

PI, INSTITUTION: K. Kinoshita, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Anodes - Carbon Materials

SYSTEMS: Low-Cost Li-Ion

BARRIER: High Cost of Li-Ion Batteries

OBJECTIVES: The primary objective is to identify a low-cost carbon (<\$10/kg) for negative electrodes in Li-ion batteries for electric and hybrid vehicles.

APPROACH: We will continue our collaboration with industry (mainly HydroQuébec) to develop low-cost carbons for Li-ion batteries. Our role will be to utilize the analytical and spectroscopic facilities at LBNL to characterize the properties of the carbons. Techniques such as high-resolution electron microscopy, scanning electron microscopy, Raman spectroscopy, X-ray diffraction analysis and thermal analysis will be used to determine the physicochemical properties of carbon. Electrochemical studies to determine the reversible capacity and irreversible capacity loss of the carbons will be conducted in laboratory-scale cells.

STATUS OCT. 1, 2000: Our results suggest that there is a strong correlation between the irreversible capacity loss and the relative fraction of edge sites associated with the graphitized carbon sample. Within the range of graphite particle sizes considered in the study, there is no significant correlation between reversible capacity and the structural parameters associated with the crystallite size (*i.e.*, L_c , L_a). These results were obtained at reasonably low charge/discharge rates. We plan to examine these effects at higher rates to determine the influence of particle size on the initial reversible capacity. The correlation with cycle life was not investigated because we are not confident that the cells available (in-house) are adequate for cycle testing. This study was conducted in collaboration with HydroQuébec.

EXPECTED STATUS SEPT. 30, 2001: We expect to identify a chemical procedure to purify natural graphite that is lower cost than thermal purification processes. The samples will be evaluated in LiPF_6 -EC-EMC, LiTFSI + cross-linked PEO, and LiBF_4 + cross-linked gel electrolytes to determine their electrochemical performance compared to baseline systems.

RELEVANT USABC GOALS: Develop low-cost carbon to meet the cost target for battery of <\$150/kWh.

MILESTONES: Complete analysis of particle-size effect on high-rate charge/discharge of flake graphite in liquid electrolyte. (03/01)

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

Low-cost natural graphite (<\$5/pound) is available, for example from mines in Canada and Brazil. However, the impurity levels are high (>1%), and the flake-like morphology is not conducive for high-rate intercalation and de-intercalation of Li^+ ions. Therefore, experiments were initiated in collaboration with HydroQuébec to investigate chemical routes to produce low-cost graphite for negative electrodes in Li-ion batteries. In addition, attrition techniques to produce low-cost graphite of the appropriate morphology are being evaluated. The aim is to produce graphite particles of average particle size of about 10 μm and with a more spherical morphology.

Chemical processing that involves fluoride ions to leach out inorganic ash is under evaluation. Improved purity of 99.9+% has been obtained by leaching with aqueous solutions containing fluoride ions from samples that contain 1.88% ash. Techniques such as air jet milling and mechanical ball milling are being used to reduce the particle size and to produce the desirable particle morphology. Chemical processing and attrition studies are conducted at HydroQuébec. The samples are evaluated at LBNL by thermal gravimetric analysis and transmission electron microscopy.

Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were performed at a heating rate of 10°C/min in air on several of the samples from HydroQuébec. The TGA/DTA studies provide a rapid and sensitive measure of the level of impurities because many of the impurities respond like catalysts and lower the onset temperature for oxidation. The results obtained with several samples indicate that an ash residue remains after oxidation, which is probably the ash that was not dissolved in the fluoride solution. Optimization of the fluoride concentration and solution temperature is being examined.

- **Further plans to meet or exceed milestones**

Milestone has been completed and reported in the first quarterly report for Fiscal Year 2001. Focus of this task will shift to development of low-cost graphite for Li-ion batteries. The effort will be conducted in collaboration with HydroQuébec.

- **Reason for changes from original milestones:** N/A

TASK STATUS REPORT

PI, INSTITUTION: G.A. Nazri and D. Curtis, University of Michigan

TASK TITLE – PROJECT: Anodes - Optimization of Anodes for Li-Ion Batteries

SYSTEMS: Low-Cost Li-Ion

BARRIER: Safety, irreversible capacity loss, and self-discharge.

OBJECTIVES: The primary objective is to improve the overall safety, cycle life, and shelf life of the Li-ion battery, through development of a low-cost surface treatment process to stabilize the anode/electrolyte interface and reduce cell impedance.

APPROACH: Our approach is to stabilize the anode/electrolyte interface to prevent self-discharge, electrolyte decomposition, and improve safety aspects of the Li-ion battery. We are engineering an artificial SEI layer on anodic materials to provide a superior thermal and chemical stability, as well as a high Li-ion conductivity for application in high-power Li-ion batteries. The work is focused on the ATD Program Gen 2 chemistry, as well as the application of EC-EMC electrolytes for sub-ambient temperature performance.

STATUS OCT. 1, 2000: We developed a Li-phosphonate based polymer stable in the operational voltage range of carbonaceous anodes with the added benefit of fire-retardant properties. We also developed a unique *in situ* technique to explore the reactivity of anode/electrolyte interfaces.

EXPECTED STATUS SEPT. 30, 2001: We expect to fully incorporate the artificial SEI layer on a carbonaceous anode, and provide test results for improved rate capability, safety, and compatibility with a lower cost and more stable electrolyte. The process developed in this research will also remove undesirable impurities and reactive surface groups from carbonaceous anodes. We expect also to provide a working mechanism and a model for the artificial SEI layer to guide the scale-up of this invention. This research work expects to provide a practical graphite anode for Li-ion technology.

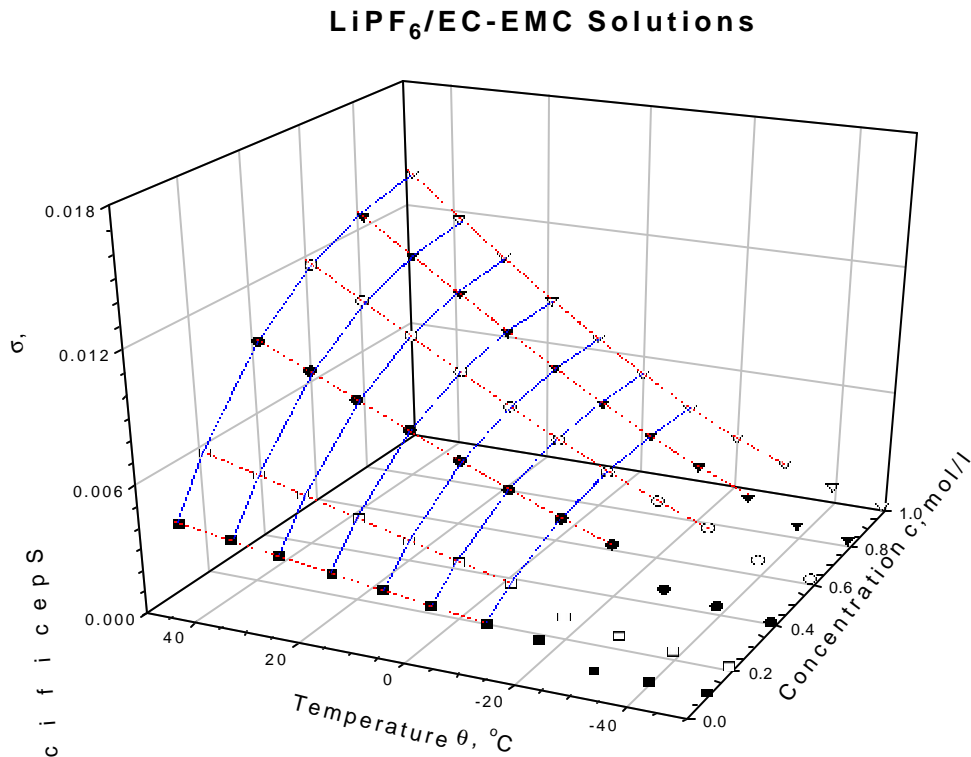
RELEVANT USABC GOALS: Improved safety of Li-ion batteries, long cycle and shelf life, compatibility for high-power batteries.

MILESTONES: Our milestones to synthesize and coat the anode with an artificial SEI, and provide performance test results are expected to be completed by the planned date, September 2001.

PROGRESS TOWARD MILESTONES

- Accomplishments toward milestone over last quarter:** A new SEI layer based on Li-Phosphonate polymer has been synthesized. Lithium transport and Li deposition through this membrane has been studied. The electrochemical stability tests have been completed, and the results indicated electrochemical stability in the voltage range of Li-ion batteries. The new SEI layer is compatible with the ATD Program Gen 2 chemistry. Long-term chemical stability of polymer in contact with highly lithiated graphite (LiC_6) has been tested, and our results show significant improvement of shelf life and reduced self-discharge of the anode. Rate capability tests of the composite graphite anodes covered with an artificial SEI have been completed.

In order to optimize low-temperature performance of the Li-ion battery, we have investigated various blends of electrolytes, and our results indicate that 1 M LiPF_6 is detrimental to the cell operation below -20°C . Recent results indicate that using EC-EMC with 0.7 M LiPF_6 may serve as the best electrolyte for both low and high temperature ranges. Figure 1 shows a sample result of the conductivity-temperature-salt concentration for the EC-EMC- LiPF_6 system.



- Further plans to meet or exceed milestones:** Our immediate plan is to complete testing of the interfacial impedance on the anode in Gen 2 chemistry and also in EC-EMC-0.7M LiPF_6 . We are also planning to test the effect of an artificial SEI layer on the anode self-discharge at elevated temperatures.

The thermal stability of the modified anode before and after charge-discharge cycles will be examined. The stability of the electrolyte during charge-discharge cycles will be studied using previously developed GC-MS and spectroscopy techniques.

- Reason for changes from original milestones:** N/A

TASK STATUS REPORT

PI, INSTITUTION: M. Thackeray, Argonne National Laboratory

TASK TITLE: Anodes - Non-Carbonaceous Materials

SYSTEMS: Low-Cost Battery

BARRIER: Cost and safety limitations of Li-ion batteries.

OBJECTIVES: To replace carbon with an alternative inexpensive anode material that will be compatible, in particular, with low-cost manganese oxide cathodes. The project also addresses the need for improved safety of Li-ion cells.

APPROACH: Our approach is to search for, characterize, and develop inexpensive intermetallic electrodes that provide an electrochemical potential a few hundred mV above the potential of metallic Li, and that provide capacities >400 mAh/g and >1000 mAh/ml (the theoretical capacities for graphite are 372 mAh/g and 818 mAh/ml, respectively). The task entails the synthesis and electrochemical evaluation of the intermetallic electrodes and their structural characterization by X-ray diffraction and spectroscopy. The reactivity of the intermetallic electrodes with the electrolyte will be determined by calorimetric techniques.

STATUS OCT. 1, 2000: We have identified intermetallic compounds with nickel-arsenide and zinc-blende structure types for possible exploitation as anodes for Li batteries. Cu_6Sn_5 and InSb were identified as test cases for the preliminary investigations of these types of materials, respectively; they yield reversible capacities of 200 mAh/g and >1000 mAh/ml for 10-15 cycles. These novel materials have exciting prospects for further development and improvement in performance.

EXPECTED STATUS SEPT. 30, 2001: Improvements in electrochemical performance from either new or modified intermetallic electrode compositions based on tin and antimony compounds will have been achieved. We expect to have improved the cycling stability of these materials with reversible capacities of 250 mAh/g and >1000 mAh/ml for 40 cycles. We will have obtained preliminary data regarding the thermal stability of the intermetallic electrodes with respect to organic-based electrolytes. We will also have gathered a more detailed understanding of the behavior of NiAs and zinc-blende electrodes in electrochemical cells.

RELEVANT USABC GOALS: 10-year life, $<20\%$ fade over a 10-year period.

MILESTONES: The primary milestone will be to increase the reversible electrochemical capacity of tin- and antimony-based electrodes from 200 to 250 mAh/g for 20 cycles by the end of April 2001, by which time preliminary calorimetric data will also have been gathered. A target of reaching a capacity of 250 mAh/g for 40 cycles by end of September 2001 has been set, by which time a greater insight of the electrochemical mechanisms of tin- and antimony-based systems will also have been gathered to enable the identification of cost-effective intermetallic electrode structures.

PROGRESS TOWARD MILESTONES

Accomplishments toward milestone over last quarter

Further characterization of Cu_6Sn_5 and substituted $\text{Cu}_{6-x}\text{M}_x\text{Sn}_5$ electrodes, where M is a transition metal, has been accomplished by *in situ* X-ray diffraction and Mossbauer analysis. In particular, we have continued to examine the role of the current collector on the electrochemical performance of the system. The latest *in situ* XRD work highlights the difference the current collector has on the performance of these electrodes. For the Cu-backed electrodes, part of the electrode capacity is delivered by a reversible reaction during which a transformation of Cu_6Sn_5 to Li_2CuSn occurs, whereas on a Ni-backed electrode, it appears that this transformation is suppressed and that the capacity is delivered predominantly by a reversible reaction in which Li is inserted into, and Cu extruded from a lithiated Li_2CuSn phase.

An *in situ* ^{119}Sn Mossbauer experiment has confirmed the reaction sequence of the Cu_6Sn_5 electrode with a Cu-backed current collector. This experiment was carried out at a few critical points in the discharge profile as the sample was being discharged. The data confirm the transformation of Cu_6Sn_5 to Li_2CuSn at 0.2V *vs.* Li, the subsequent formation of $\text{Li}_{4.4}\text{Sn}$ at ~ 0.01 V, and the reformation of Li_2CuSn and Cu_6Sn_5 during charge. The parent compound, Cu_6Sn_5 , appears to be completely regenerated by 1.0 V, but contains more local disorder than the initial structure.

We have also focused our efforts on increasing the capacity of Cu_6Sn_5 electrodes above 200 mAh/g by using substituted materials, *e.g.*, FeCu_5Sn_5 . Slightly improved capacities over pure Cu_6Sn_5 have been achieved with FeCu_5Sn_5 electrodes, using both Cu and Ni current collectors, when cycled twenty times between 1.2 V and either 0.1 or 0.05 V as shown in Fig. 1. Of particular note is that a higher capacity is obtained from the FeCu_5Sn_5 electrode when the cut-off voltage is set at 0.1 V rather than 0.05 V. Work is being continued in attempts to improve the capacity retention of these copper-tin materials during cycling.

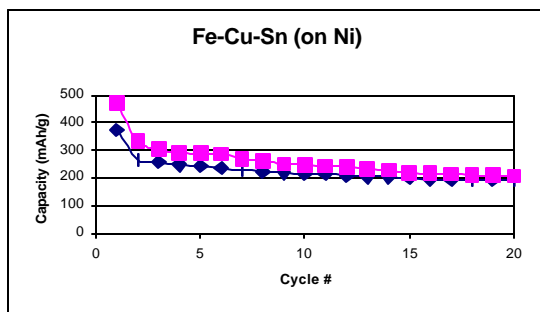


Figure 1. Capacity *vs.* cycle no. for FeCu_5Sn_5 electrodes on Ni current collector (squares indicate the capacity to 0.10 V, diamonds to 0.05 V)

We are collaborating with US industry and have collected preliminary calorimetric data to determine the reactivity of the intermetallic electrodes with organic-based electrolytes.

Further plans to meet or exceed milestones: N/A

Reason for changes from original milestones: N/A

TASK STATUS REPORT

PI, INSTITUTION: M.S. Whittingham, SUNY at Binghamton

TASK TITLE - PROJECT: Anodes - Novel Materials

SYSTEMS: Low-Cost Li-Ion Battery and Gel Battery.

BARRIER: Cost, safety and volumetric capacity limitations of lithium-ion batteries

OBJECTIVES: To replace the presently used carbon anodes with safer materials that will be compatible with manganese oxide cathodes and the associated electrolyte.

APPROACH: Our anode approach is to explore, synthesize, characterize, and develop inexpensive materials that have a potential about 500 mV above that of pure Li (to minimize the risk of Li plating and thus enhance safety) and have higher volumetric energy densities than carbon. We will place emphasis on simple metal alloys. All materials will be evaluated electrochemically in a variety of cell configurations, and for thermal and kinetic stability.

STATUS OCT. 1, 2000: We have determined that vanadium and manganese oxides, in their highest oxidation states, are probably not prime candidates. Pure aluminum was found to have a high capacity and to react readily with Li, but its capacity faded rapidly on cycling. Some simple binary alloys of aluminum and of tin have been identified and are being evaluated.

EXPECTED STATUS SEPT. 30, 2001: We expect to improve the electrochemical performance of the materials identified, to have completed a survey of all Al-based binary systems and their reactivity with Li, and to have identified several additional non-Al binary alloys. We will complete a study of the lower-valent MnV_2O_5 oxide.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestone is to identify, by September 2001, a new simple material (a binary alloy) that has the potential of higher volumetric capacity than carbon at about 0.5 V relative to pure Li. In addition, we will identify all known Al binary alloys and their ability to react with Li by August 2001, and our assessment of MnV_2O_5 as an anode material will be completed by April 2001.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

We are investigating several manganese-based anodes, as they should be immune to poisoning by manganese species migrating from the cathode. These include both “alloy” systems and oxides. We have synthesized the tin manganese compound, MnSn_2 in a pure state and evaluated it in a cell vs. Li metal. The discharge and charge curves are reproducible over the first several cycles; the charging voltage of about 0.3 to 0.4 V establishes a safety region, and the discharge potential of about 0.6 V in an oxide cell does not result in excessive energy loss. The capacity is high and retained over the first five cycles as shown below, but decreases rapidly thereafter just as reported by Dahn *et al.* We are presently investigating means for reducing capacity loss, which is likely related to tin sintering.

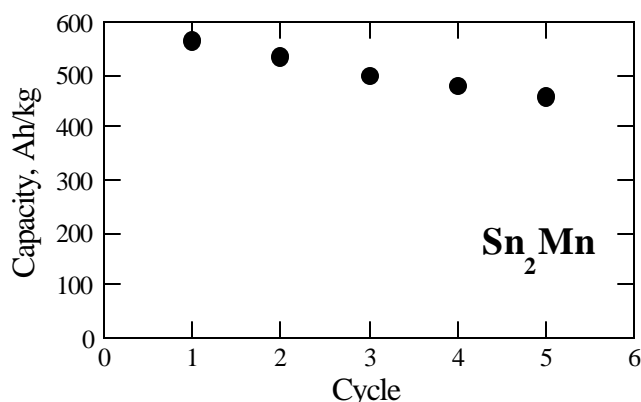


Figure 1. Capacity of a tin-manganese anode cycled in a lithium cell.

French workers studied MnV_2O_6 and found positive results but with a low storage capacity; other French workers have noted higher levels of success using nano-sized oxide materials. MnV_2O_5 , a material first synthesized by us, should have a higher storage capacity because of its lower oxygen content. We have synthesized a sample for evaluation as an oxide anode, and our results indicate insufficient capacity to merit further study.

There is a large effort at Binghamton investigating lead free solders for electronics packaging applications. We are beginning discussions with them on their tin-based solders, which might possibly lead to attractive tin-based anode materials.

We have received delivery of a button cell set-up, which will allow for more reproducible cell systems. We will visit NRC Ottawa next month for training in its use.

- **Further plans to meet or exceed milestones:** None.
- **Reason for changes from original milestones:** N/A

Presentation

“Aluminum based anode materials for rechargeable batteries,” S. Yang, P.Y. Zavalij and M.S. Whittingham at the Materials Research Society National Meeting, Boston, December 2000. (to be published in meeting proceedings).

BATT TASK 3 ELECTROLYTES

TASK STATUS REPORT

PI, INSTITUTION: J. Kerr, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Electrolytes - R&D for Advanced Lithium Batteries

SYSTEMS: Li/Polymer and Low-Cost Li-Ion

BARRIERS: Short Li battery lifetimes, poor ambient-temperature performance for polymer electrolytes, and low energy and power densities as a result of polymer instability to 4-V cathodes.

OBJECTIVES:

- Determine the feasibility of the Li metal electrode with organic electrolytes and provide operating conditions that prevent dendrite growth.
- Determine the limitations on Li-ion transport in polymer electrolytes and composite electrodes and develop new materials capable of ambient-temperature operation with Li metal.
- Determine the limits of stability of organic electrolytes at high-voltage cathode materials (4 V) and develop materials and methods to increase stability.

APPROACH: Through a balance of synthesis, analysis, and modeling, a physical organic chemistry approach is taken to electrolyte design, thereby ensuring that not only are the sources of poor performance and failure pinpointed but the problem can be corrected through the materials design and synthesis capabilities thereby developed.

STATUS OCT. 1, 2000: Polymer synthesis capability has been established that facilitates the production of linear and branched polymer networks for use in Li/polymer batteries and polymer gel Li-ion systems. New polymers with significantly higher conductivities are now available as are polymer systems with higher voltage stabilities than PEO.

EXPECTED STATUS SEPT. 30, 2001: We expect to complete a study of the effects of mechanical, chemical, and transport properties of polymer electrolytes on dendrite growth at Li metal electrodes that will provide data to allow the system to be accurately modeled. We expect to prepare and test polymer electrolytes with room-temperature performance and to define the upper limits of ion transport for polymer electrolytes. We expect to determine the practical cathode stabilities of polymer electrolytes with adequate transport properties.

RELEVANT USABC GOALS: 10 year life, <20% capacity fade over a 10-year period, 1000 cycles, operating environment -40 to 65°C, specific energy >170 Wh/kg, specific power >300 W/kg, <150\$/kWh @ 20K/year.

MILESTONES:

1. Determine electrolyte properties that inhibit dendrite growth (September 30, 2001).
2. Determine the limits of Li ion mobility in polymer electrolytes (September 30, 2001).
3. Prepare bulk materials (100g) for testing in the BATT Li polymer (April 15, 2001) and low-cost Li-ion test systems (June 30, 2001).

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 over last quarter:** Several batches (>20g each) of comb-branch and linear cross-linkable polymers have been prepared, purified and characterized by GPC. Discussions have been initiated with a polymer manufacturer to investigate the behavior of commercially available materials.
 - **Further plans to meet or exceed milestones:** Preparation, characterization, and testing of cross-linked polymer membranes to determine how transport properties, mechanical properties, and chemical reactivity promotes or inhibits dendrite growth.
 - **Reason for changes from original milestone:** Progress towards this milestone has slipped due to lack of staff. Industry values the skills that are required for this task and consequently the staff is in high demand. However, replacements have been found and it is expected that the lost time will be fully made up.
-
- **Accomplishments toward milestone 2 over last quarter:** Lithium-ion mobility in polymer electrolytes is governed by the solvation of the Li ion, ion-pairing to the anions, and the polymer architecture. Further conductivity measurements on new polymers with solvating groups other than ethylene oxide have been carried out. More material has been synthesized to allow further testing of macrocyclic groups, linear comb-branch, and linear polymers. The synthetic method is less than optimal and efforts have been continued to find better syntheses. New equipment (HPLC and GC/MS) has been installed.
 - **Further plans to meet or exceed milestones:** Collaboration with modeling groups in the BATT program and in the DOE Office of Science program indicates that the approach will result in room-temperature polymer electrolytes. Synthesis and testing of these materials are underway. It is expected that higher conductivities than previously expected may yet be achieved, and it is planned to demonstrate room-temperature performance for full Li/polymer/V₆O₁₃ cells in the coming quarter.
 - **Reason for changes from original milestone:** Plans for this milestone have fallen behind schedule due to unexpected reactivity of the polymers that leads to cross-linking and also due to the staff shortage.
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- **Accomplishments toward milestone 3 over last quarter:** Large amounts (>100gm) of polymers are under preparation for testing in the BATT Li/polymer system and the low-cost polymer gel system. Samples of PEO have been obtained from manufacturers. and arrangements made with battery companies to facilitate the preparation of the polymer systems in practical and credible battery test systems.
 - **Further plans to meet or exceed milestones:** Polymer electrolytes will be formulated with salts and electrode components to provide separators and composite electrodes. Appropriate transport and mechanical characterization will be carried out in addition to electrochemical cell testing. Scale up to 100 cm² area is planned.
 - **Reason for changes from original milestone:** Unexpected cross-linking of polymers has impeded progress. This may be due to poor control over molecular weight in addition to photochemical and thermal reactions of the ether units. New equipment is helping to untangle this problem. A collaboration with a polymer manufacturer has been initiated to provide cross-linked PEO materials in large quantities. It is expected that this milestone will be met by May 15, 2001.

TASK STATUS REPORT

PI, INSTITUTION: M. Ratner, Northwestern University

TASK TITLE - PROJECT: Electrolytes - Modeling of Lithium/Polymer-Electrolyte Batteries

SYSTEMS: Lithium/Polymer, Gel Electrolyte

BARRIER: Reduced power density in lithium batteries.

OBJECTIVES: Our primary objective is the achievement of modeling-based design protocols for polymer electrolytes and polymer gel electrolytes, in Li metal batteries.

APPROACH: This purely theoretical work uses both ab-initio electronic structure calculations to optimize anionic components of the battery electrolyte, and dynamic Monte Carlo calculations to understand and model the effects of polymer physical properties (including gelation and charge density) on the ionic conductivity, and therefore the power density, of electrolyte batteries.

STATUS OCTOBER 2, 2000: We had completed the electronic structure work, suggesting modalities for optimized anionic centers (delocalized charge, chemically “soft” centers, aluminosilicate rather than aluminate). Monte Carlo applications on the optimization of the phase diagram are beginning.

EXPECTED STATUS SEPTEMBER 30, 2001: We should have completed the phase diagrams for the comb/tooth polyelectrolyte (single-charge conductor) Li battery electrolyte. We will also have begun generalized dynamic percolation models for optimization of the gel component in gel electrolyte batteries, and analyzed the possible percolation pathways for such structures.

RELEVANT USABC GOALS: 10-year life, conductivity of 10^{-3} S/cm for stable electrolytes, 10^{-4} S/cm for single-charge conductors.

MILESTONES: We have completed the milestone on electronic structure modeling. The current challenging milestone is, by June of 2001, to have completed the phase diagrams for the percentage of charge density (Li bearing) vs. neutral (polyether) side chains on the soft backbone of designed polymer batteries.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

Investigator has indicated that he will not seek renewal of his LBNL subcontract. No report was received.

- **Further plans to meet or exceed milestones:**

By June of 2001, we should have complete results for the homogeneous case. The milestone for the remainder of 2001 will involve the gel electrolytes.

- **Reason for changes from original milestones:**

We had proposed a static/dynamic percolation picture for optimizing the percentage of gel agent. Work on this will not begin until the phase diagrams are completed: we anticipate completing this part by January 2002.

TASK STATUS REPORT

PI, INSTITUTION: S.A. Khan, P.S. Fedkiw, North Carolina State University; G.L. Baker, Michigan State University

TASK TITLE - PROJECT: Electrolytes - Composite Polymer Electrolytes for Lithium and Lithium-Ion Batteries

SYSTEMS: Li/Polymer

BARRIER: Short lithium battery lifetimes and high costs.

OBJECTIVES: The ultimate objectives are to develop composite polymer electrolytes that are low-cost, have high conductivities, impart electrode-electrolyte interfacial stability, and yield long cycle life.

APPROACH: Our approach is to use surface-functionalized fumed silica fillers in BATT-baseline systems to determine the effects of filler type and concentration on interfacial stability and cell cycling. We intend to correlate these electrochemical characteristics with mechanical properties and materials chemistry (*e.g.*, silica-type or PEO-type, synthesized by Baker or Kerr, respectively). Data to be collected include modulus, ionic conductivity, Li cycling efficiency, Li-electrolyte interfacial resistance, and full-cell cycling capacity using 3-V cathodes.

STATUS OCT. 1, 2000: We established that fumed silica-based composite electrolytes with low-molecular weight PEOs exhibit conductivities exceeding 10^{-3} S/cm at 25°C; have electrochemical properties (Li transference number, conductivity) decoupled from mechanical properties, thus providing a range of mechanical modulus (as high as 10^6 Pa); and, the presence of fumed silica enhances Li-electrolyte interfacial stability, although the extent and mechanism remain to be determined.

EXPECTED STATUS SEPT. 30, 2001: We expect to determine how fumed silica (hydrophobic R805 and hydrophilic A200) affect full-cell cycling using vanadium-based, 3-V cathodes and baseline PEO-type materials in coin cells. We also expect to identify to what extent fumed silica enhances interfacial stability in low-molecular-weight PEOs and begin extending the analysis to base-line PEO materials. We expect to characterize how interfacial stability is related to the mechanical properties, working in close collaboration with J. Kerr.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestone to determine the effects of fumed silica (hydrophobic R805 and hydrophilic A200) on full-cell cycling and interfacial stability is expected to be completed by September 2001.

PROGRESS TOWARD MILESTONES

- Accomplishments toward milestone over last quarter:** Preliminary full-cell cycling data of rechargeable Li batteries using 3-V V_6O_{13} based cathodes are shown in Fig. 1. V_6O_{13} cathodes consist of 75 wt% V_6O_{13} (Kerr-McGee), 20 wt% graphite SFG 15 (Timcal), and 5 wt% poly(vinylidene fluoride) (PVDF) binder (Kynar). Carbon fiber was used as the current collector. Three types of electrolytes were used for the comparison: the base liquid electrolyte with LiTFSI in PEG-dm (250) (Li:O=1:20), 10 wt.% R805 (octyl-modified) composite polymer electrolyte (CPE), and 10 wt% A200 (with hydroxyl group) CPE. Cells were discharged at C/15 (0.4 mA/cm^2) to 1.8 V and re-charged at C/30 (0.2 mA/cm^2) to 3.0 V. Cell capacities of liquid electrolyte and composites are comparable initially with a slightly higher capacity of liquid electrolyte. Although all cells show a decrease of capacity with increasing cycle number, the presence of fumed silica appears to diminish capacity fading: cell capacities after 20 cycles were 42 mAh/g ($0.8\text{Li}/V_6O_{13}$) for liquid electrolyte, 100 mAh/g ($1.9\text{Li}/V_6O_{13}$) for 10% R805 CPE, and 116 mAh/g ($2.2\text{Li}/V_6O_{13}$) for 10% A200 CPE, respectively. We are presently exploring causes for the capacity fade.

We are continuing our research on understanding the mechanism of ion transport in our composite electrolytes. Given that the silica filler has little effect on ionic transport, we can now focus on only the liquid electrolyte components for understanding the role of salt. Figure 2 displays a compilation of data for LiTFSI in PEGdm(250) with no fumed silica. Initially the conductivity increases due to more charge carriers being present. However, a decrease occurs due to a loss of mobility of the ions as more ions are added to the system. The increase in viscosity coupled with the decreasing diffusivity of the PEGdm suggests loss of segmental motion or an overall decrease in charge-transport rate.

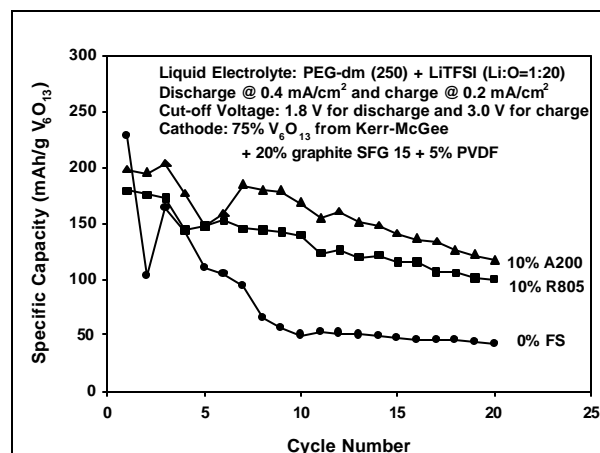


Figure 1. Preliminary full-cell cycling results using V_6O_{13} cathodes with liquid electrolyte, 10% R805, and 10% A200 CPEs

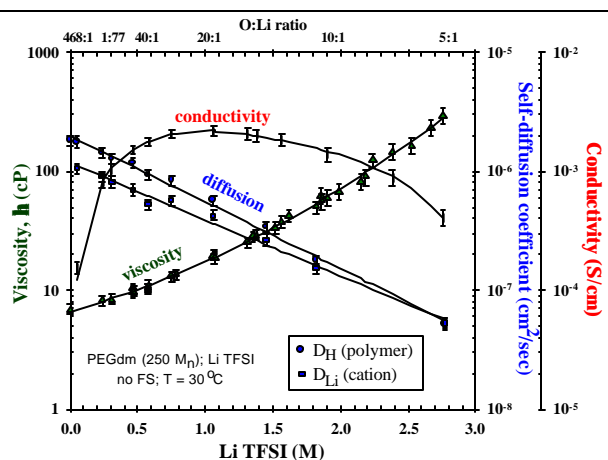


Figure 2. Effect of lithium salt on ion transport. Lines are only meant to guide eyes and do not represent any theory or models

- Further plans to meet or exceed milestones:** We plan to hire a post-doc starting May 1, 2001 to continue full-cell cycling using vanadium-based, 3-V cathodes. We will also focus on interfacial stability studies using base-line materials with fumed silica. In conjunction with J. Kerr, we will also focus on correlating mechanical properties to interfacial stability.

- Reason for changes from original milestones:** N/A

TASK STATUS REPORT

PI, INSTITUTION: D.F. Shriver, S. Vaynman, Northwestern University

TASK TITLE - PROJECT: Electrolytes - Highly Conductive Polyelectrolyte-Containing Rigid Polymers

SYSTEMS: Li/Polymer

BARRIER: Low ionic conductivity of the polymer electrolyte, electrochemical instability of the polymer electrolyte toward Li electrodes.

OBJECTIVES: The primary objective is to synthesize and test a new class of highly ionic-conductive, rigid polymer electrolytes for rechargeable Li batteries.

APPROACH: Our approach is to modify the highly ion-conductive rigid polymer electrolytes previously synthesized at Northwestern University by replacing electrochemically unstable carboxy groups with more inert oxygen-rich functional groups such as sulfones, thus increasing the stability of the electrolyte toward the Li electrode. If this or related instabilities with sulfone-containing polymer electrolytes are encountered, we will prepare new polymer electrolytes. One such possibility is a bilayer electrolyte with an oxidation-resistant fluorocarbon backbone on one side and a reduction-resistant hydrocarbon or hydrocarbon ether backbone on the surface in contact with the Li electrode. At least two polymer-salt complexes and polyelectrolytes will be synthesized, and their properties will be measured. These electrolytes will be tested in Li cells. Before polymers are synthesized we will test the stability of the small-molecule analogs of the polymers in contact with Li metal.

STATUS OCT. 1, 2000: We synthesized highly conductive rigid polymer electrolytes that contain functional groups such as carboxy and sulfone and tested them in cells. Polymer-salt complexes that contain carboxy groups have high ionic conductivity ($\sim 10^{-4}$ S/cm at room temperature), but are unstable toward Li. The ionic conductivity of a recently synthesized polymer-salt complex that contains sulfone functional groups is lower ($\sim 5 \times 10^{-6}$ S/cm at room temperature), but the stability toward Li is much higher than that of polymer-salt complexes that contain carboxy groups.

EXPECTED STATUS SEPT. 30, 2001: We expect to synthesize and test in cells a number of sulfone-containing rigid polymer electrolytes and polyelectrolytes that display favorable ionic conductivity and good electrochemical stability toward battery components. Also, we expect to scale up the synthesis of the most promising electrolyte(s) and send them to LBNL for large-scale testing.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestones are:

1. To synthesize and test promising polymer systems by 6/2001 with the goal of conductivity higher than 10^{-4} S/cm at room temperature. The resistivity of the Li/polymer electrolyte cell should not increase more than twice during the first week of testing.
2. To scale-up the synthesis of the most promising polymer electrolyte and to send it by 10/2001 to LBNL for cell fabrication and testing.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 over last quarter**

Our project focuses on:

- a. chemical synthesis of highly ion-conductive rigid polymer electrolytes,
- b. study of the ion-transport properties of these electrolytes,
- c. investigation of interactions at the Li electrode/polymer electrolyte interface,
- d. testing of the electrolyte in a battery configuration.

During the last quarter we continued testing the polyarylsulfone (a) in a battery configuration and we synthesized polysulfone (b) (Fig 1). The capacity of the cell containing the polysulfone (a) - lithium triflate polymer electrolyte was high at low current density discharge, however an increase in current density significantly reduced the cell capacity, owing to low ionic conductivity of the polyarylsulfone (a) - containing polymer electrolyte (ca. 5×10^{-6} S/cm at room temperature).

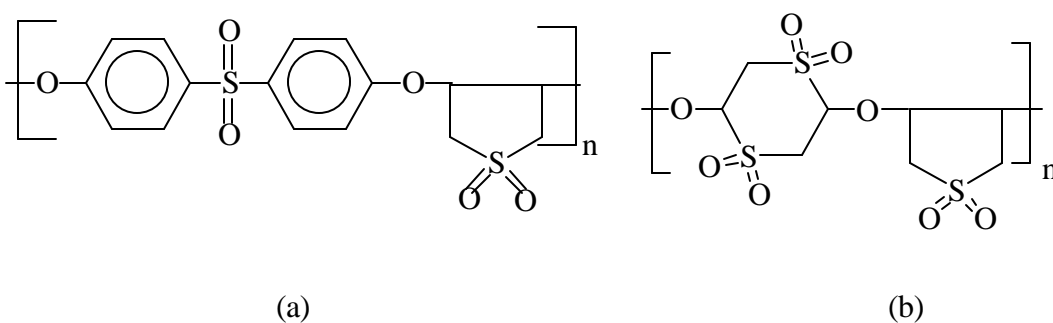


Figure 1. Structure of polysulfones under investigation.

We continued to work out synthetic routes to sulfone-containing polymer (b). At the present time a low-molecular-weight polymer has been synthesized, which is not solid at room temperature. Modifications of the synthetic routes are being made to increase the molecular weight of the polymer.

We anticipate that when doped with salt, polymer (b) will display higher ionic conductivity than that of polymer (a), because the polymer (b) has a higher density of cation coordinating sites than (a). We also expect high stability of polymer (b) toward Li.

- **Further plans to meet or exceed milestones**

We expect to meet our milestone by synthesizing the sulfone-containing polymer (b) soon and then testing its stability toward Li. This will be followed by the testing of polysulfone/salt complex in a Li/polymer electrolyte/ Li_xMnO_2 cell.

- **Reason for changes from original milestones:** N/A

TASK STATUS REPORT

PI, INSTITUTION: K. Kinoshita, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Electrolytes - Electrolyte Additives

SYSTEMS: Low-Cost Li-Ion

BARRIER: Safety of Li-Ion Batteries

OBJECTIVES: The primary objective is to identify chemical additives that improve the safety of nonaqueous electrolytes for Li-ion batteries by stabilizing the SEI layer on carbon.

APPROACH: A study will be undertaken to identify suitable additives that function as a radical trap for the radical anions produced by solvent reduction. We propose to use this concept to identify species that are incorporated in the SEI layer to improve its stability. This type of reaction product will be evaluated as additives in gel and liquid electrolytes. Based on our studies of reaction products obtained by thermal decomposition of the electrolyte, compounds that decompose to form polyether and polycarbonate oligomers will be studied as additives. Electrochemical evaluation of additives to determine the reversible and irreversible capacity loss will be conducted in coin cells using the baseline liquid or gel electrolytes. TEM and AFM will be used to study the effect of additives on the thickness and structure of the SEI layer and the irreversible capacity loss of carbon electrodes. Thermal analysis studies will be used to determine the thermal stability of carbon electrodes containing a SEI layer.

STATUS OCT. 1, 2000: Experiments were initiated to determine the thermal stability of a baseline electrolyte [1 M LiPF₆ in a mixture of 1:1 EC/DMC]. The electrolyte was heated to 85°C, and samples were removed periodically for analysis by gas chromatography (GC). The GC trace from the electrolyte mixture shows two clearly separate solvent peaks for DMC (5-min retention time) and EC (about 14.1-min retention time) as well as a large new peak at 13.8-min retention time and several others of lower intensity. The peak intensity for EC decreases as a function of storage time, indicative of the gradual decomposition of EC at 85°C. On the other hand, the GC signal for DMC remains essentially constant in intensity, indicating that DMC is stable during storage at 85°C. The major new compound was identified as diethyl 2,5 dioxahexane carboxylate (DEDOHC), which increases with time of storage at 85°C.

EXPECTED STATUS SEPT. 30, 2001: We expect to identify a chemical additive that enhances the thermal stability of the SEI layer on carbon. The additives will be evaluated in a liquid electrolyte to determine their electrochemical performance compared to baseline systems.

RELEVANT USABC GOALS: Identify additives that improve the safety of Li-ion batteries.

MILESTONES:

1. Identify desired structural features of additives that enhance SEI properties (12/00).
2. Evaluate the effect of polycarbonates as additives for improving the thermal stability of the SEI layer on carbon electrodes (9/01).

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 over last quarter:**

Complete. Described in FY01 first quarterly report.

- **Further plans to meet or exceed milestone:** N/A
- **Reason for changes from original milestone:** N/A

- **Accomplishments toward milestone 2 over last quarter:**

The polyether carbonates $(\text{CH}_2\text{CH}_2\text{O})_m\text{COO})_n$ $[\text{PE}_3\text{C}]$ were identified as possible decomposition products when 1 M LiPF_6 in a mixture of 1:1 EC/DMC heated to 85°C . The PE_3C should simulate the end product that may be produced during the formation of the SEI layer (electrolyte decomposition) at the anode. The Illinois Institute of Technology (IIT) has evaluated PE_3C as an additive in 2016 coin cells (Li/carbon) containing 1 M LiPF_6 and EC+DEC. The anode from the Generation-1 chemistry in the ATD Program (MCMB+ 6% SFG) was used. Electrochemical studies showed that the presence of the additive in the electrolyte has a very small effect on the reversible capacity but produces a higher irreversible capacity loss. After the electrochemical studies were completed, the coin cells were disassembled and the negative electrodes were removed for examination by transmission electron microscopy. There was no obvious difference in the solid electrolyte interphase (SEI) layer that was observed on graphite removed from cells with or without PE_3C added. Based on these preliminary results, adding PE_3C to the electrolyte had no benefit in reducing the irreversible capacity loss or changing the structure of the SEI layer. However, the effect of PE_3C on the thermal stability of the negative electrode was not investigated.

- **Further plans to meet or exceed milestone:**

Experiments will be conducted with additives that are expected to decompose during the initial intercalation (charge) of carbon electrodes in the baseline electrolyte. The addition of PE_3C to the electrolyte has so far not provided evidence that it has a beneficial effect on the irreversible capacity loss or the structure of the SEI layer. However the thermal stability of the SEI layer formed with the PE_3C additive in the electrolyte has not been investigated. Thermal studies will be considered when a post-doctoral fellow arrives.

- **Reason for changes from original milestone:** N/A

TASK STATUS REPORT

PI, INSTITUTION: J. Prakash, Illinois Institute of Technology

TASK TITLE - PROJECT: Electrolytes - Nonflammable Electrolytes and Thermal Characterization

SYSTEMS: Li/Polymer and Low-Cost Li-Ion

BARRIER: Thermal safety

OBJECTIVES: The goal of this proposal is to assist DOE/BATT in developing advanced high-performance Li-ion cells for electric and hybrid vehicles. The objectives of this project are: (1) to develop nonflammable electrolytes with high flash point ($>100^{\circ}\text{C}$), ionic conductivity (10^{-3} S/cm), and wider voltage window (0-5 V vs. Li); and (2) to evaluate anode and cathode (being developed in the BATT Program) materials in coin cells using thermal diagnostic methods.

APPROACH: Our research approach will include (1) the development of thermally stable and nonflammable electrolytes to provide safety and (2) thermal diagnostic studies of the baseline Li-polymer and low-cost Li-ion cells using differential scanning calorimetry (DSC), isothermal microcalorimetry (IMC), and accelerated rate calorimetry (ARC) in order to understand the degradation, failure, and safety mechanisms.

STATUS OCT. 1, 2000: We completed the synthesis of the flame retardant (FR) hexa-methoxy-tri-aza-phosphazene $\text{N}_3\text{P}_3 [\text{OCH}_3]_6$ and supplied 10 grams of this material to the ATD Program (ANL and PolyStor) for further testing in PNGV Li-ion cells. We also completed the thermal and electrochemical characterization of this FR additive in Li-ion cells using cyclic voltammetry, AC-impedance, cell cycling, DSC, and ARC.

EXPECTED STATUS SEPT. 30, 2001: We expect to synthesize two flame-retardant additives, hexa-ethoxy-tri-aza-phosphazene (HETAP) and urea-diphosphonate (URDP), and characterize their electrochemical and thermal behavior in low-cost Li-ion cells. We also expect to complete the synthesis and characterization of two thermally stable and corrosion-resistant modified imide salts $\text{LiN}(\text{SO}_2\text{X})_2$ ($\text{X} = -\text{CF}(\text{CF}_3)_2$ and $-\text{C}(\text{CF}_3)_3$). In addition, we expect to characterize the thermal behavior of Li-ion cells containing graphite and Sn-based anodes, $\text{LiAl}_{0.05}\text{Ni}_{0.8}\text{Co}_{0.15}\text{O}_2$ and $\text{Li}_{1.02}\text{Al}_{0.25}\text{Mn}_{1.75}\text{O}_{3.92}\text{S}_{0.03}$ cathode in $\text{LiPF}_6\text{-EC-EMC}$ and LiBF_4 + cross-linked gel electrolyte.

RELEVANT USABC GOALS: Thermal and fire safety of the EV batteries under normal and abusive conditions.

MILESTONES:

1. The scale-up synthesis of the FR additive HMTAP and the thermal characterization of the FR additive HETAP are expected to be completed by the planned date of April 2001.
2. The thermal characterization of graphite anode (for comparison purposes) using IMC and DSC is also expected to be completed by April 2001.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 over last quarter:** During last quarter, we completed the synthesis of a new FR (HETAP) and characterized this additive for its electrochemical and thermal properties using cyclic voltammetry, AC-impedance, and accelerated rate calorimetry (ARC). Initial thermal behavior of the new FR additive look promising (Fig. 1).
- **Further plans to meet or exceed milestone:** N/A
- **Reason for changes from original milestone:** N/A
- **Accomplishments toward milestone 2 over last quarter:** We also completed the synthesis of the flame retardant (FR) $\text{N}_3\text{P}_3[\text{OCH}_3]_6$ (HMTAP) and supplied 15 grams of this material to the ATD group (Argonne National Lab) for further evaluation in PNGV Li-ion cells. The effect of the FR on ATD Gen 1 full sealed-cells is shown in Fig. 2. It can be seen that the presence of 5-wt% HMTAP shifts the onset of thermal runaway by about 20 to 25°C. However, the SHR at temperatures beyond 230°C was found to increase in presence of HMTAP as shown in Fig. 2.

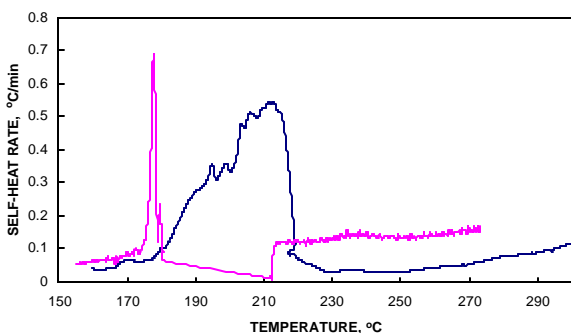


Figure 1. ARC measurement of HETAP in Li-ion electrolyte (Blue: 0% HETAP, Pink: 5% HETAP)

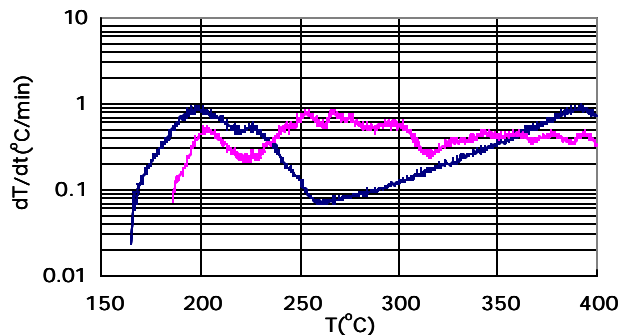


Figure 2. ARC studies. (Blue line: Gen-1 cell without HMTAP, Pink line: Gen-1 cell with 5% HMTAP)

- **Further plans to meet or exceed milestone:** We plan to complete the mechanistic investigations on HMTAP in order to understand the catalytic reaction of the FR additive with the electrode/electrolyte especially at higher temperatures by June 2001. We will also synthesize and characterize a new flame retardant additive urea-diphosphonate (URDP) for its electrochemical and thermal properties in Li-ion cells June 2001. We have initiated the thermal characterization of PNGV Gen-1 graphite anode (for comparison purposes) using isothermal microcalorimetry and DSC and plan to complete by May 2001.
- **Reason for changes from original milestone:** The detailed investigations have shown that the presence of FR additive HMTAP increases the onset of the thermal runaway of the Li-ion cells by more than 25°C (see Fig. 2), which is encouraging for the safety. However, the SHR at temperatures beyond 265°C was found to increase in presence of HMTAP. In order to address the issue of SHR at higher temperatures and to meet the milestone (FR additives for Li-ion batteries), we are now synthesizing new FR additives (HETAP and URDP) with reduced SHR at higher temperatures as a possible replacement for HMTAP. In addition, we are also carrying out thermal diagnostic studies of the Li-polymer and low-cost Li-ion cells containing the FR additives using differential scanning calorimetry (DSC), isothermal microcalorimetry (IMC), and accelerated rate calorimetry (ARC) in order to understand the degradation, failure, and safety mechanisms.

Presentation: "Studies on electrochemical and thermal properties of Li-ion battery electrolytes with different salts," Abst. 143, 198th ECS Meeting, Phoenix, AZ, Oct. 22-27, 2000.

TASK STATUS REPORT

PI, INSTITUTION: A. McEwen, Covalent Associates, Inc.

TASK TITLE - PROJECT: Electrolytes - Nonflammable Electrolytes for Li-ion Batteries

SYSTEMS: High-performance nonflammable electrolytes for Li-ion batteries

BARRIER: Limited thermal stability of Li-ion electrolytes

OBJECTIVES: The primary objective is to develop nonflammable electrolytes for Li-ion batteries to meet DOE safety goals. These electrolytes will be optimized for the cell objectives for liquid electrolytes outlined by the BATT program.

APPROACH: Our approach is to synthesize new ionic liquids and to formulate these into Li-ion electrolytes with the addition of Li salts and common solvents. We determine their suitability by measuring conductivity, Li intercalation, and cycle life of half-cell and full-cell batteries using these new electrolytes. Flammability and flashpoint of the electrolytes are determined.

STATUS OCT. 1, 2000: We demonstrated a long-lived Li-ion battery using a nonflammable ionic-liquid-based electrolyte. Over 40 cycles were obtained from a graphite/LiCoO₂ coin cell battery.

EXPECTED STATUS SEPT. 30, 2001: We expect to identify an optimum nonflammable ionic liquid formulation for Li-ion battery electrolytes based on performance and price. The compatibility of these ionic liquid electrolytes will be determined with the systems of interest. We will investigate alternative cathodes and anodes from the LiCoO₂ cathode and Li and graphite anode we are working presently with in our feasibility studies. Specifically, the LiFePO₄ and Li_{1.02}Al_{0.25}Mn_{1.75}O_{3.92}S_{0.03} positive electrode and Sn-based negative electrode will be assessed with our novel nonflammable electrolytes. We will also assess the performance of the inexpensive lithium salt LiTFSI in the ionic liquid formulations.

RELEVANT USABC GOALS: High-performance nonflammable electrolytes/low-cost electrolytes.

MILESTONES: Our major milestone to demonstrate a nonflammable Li-ion electrolyte based on ionic-liquid technology should be completed by the planned date of April 2001.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

Contract ended April 30, 2001. Investigator is preparing final contract report.

- **Further plans to meet or exceed milestones:** N/A
- **Reason for changes from original milestones:** N/A

TASK STATUS REPORT

PI, INSTITUTION: K. Wheeler, Delaware State University

TASK TITLE - PROJECT: Electrolytes - Development of Novel Sulfone Based Electrolytes for Rechargeable Lithium Battery Applications

SYSTEMS: Li/Polymer

BARRIER: Electrochemical Stability

OBJECTIVES: The primary objectives are to fabricate and determine the structure-electrochemical stability properties of a series of sulfone cross-linked PEO polymers.

APPROACH: Our approach is to utilize standard organic preparative methods to synthesize a homologous series of sulfone cross-linked PEO polymers. Synthetic strategies include condensation of PEG's with 3-chloro-2-chloromethyl-1-propene with alkali conditions to produce the expected co-block 1D polyethers. Further reaction of the polycondensate will follow a radical initiated cross-linking with divinylsulfone to give the expected sulfone cross-linked PEO polymers. Additional studies include determination of the structural features and the electrochemical stabilities of these polymer electrolytes with cells that use platinum microdisc (working) and Li strip (reference and counter) electrodes.

STATUS OCT. 1, 2000: We have prepared and characterized three sulfone cross-linked PEO polymers based on 400, 2000, and 4600 MW PEG precursors and defined relationships between electrolyte composition and electrochemical stability.

EXPECTED STATUS SEPT. 30, 2001: We expect to characterize the electrochemical susceptibility of polymeric sulfone cross-linked PEO/LiIm electrolytes under varying conditions and to identify key pathways of degradation of these electrolytic systems. We expect to determine the role of the sulfone functionality as related to electrolyte performance.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: The major milestone of the program centers on improving preparative methods and determining the influence of key chemical features of the sulfone and polymeric units to the electrochemical processes. Milestone is expected to be achieved by April 2001.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

Project efforts during the reporting period focused on the analysis of cyclic voltammogram data collected for previously synthesized sulfone cross-linked polyethylene oxide polymers. Inspection of the voltammograms acquired from these studies revealed the onset of polymer decomposition at ~ 4.0 V vs. Li and shows stability under reversible electrochemical processing. Electrochemical stability of these polymeric materials originates from the projects design strategy to synthesize effective electrolytic materials constructed of (i) amorphous PEO frameworks and (ii) electrochemically resistant sulfone functional groups.

- **Further plans to meet or exceed milestones**

None.

Reason for changes from original milestones:

Subcontract expiration in May 2001 has necessitated completion of program's task objectives and thus our efforts have also concentrated on the conclusion of several ongoing experiments related to the project.

BATT TASK 4 CATHODES

TASK STATUS REPORT

PI, INSTITUTION: M. Thackeray, Argonne National Laboratory

TASK TITLE: Cathodes - Novel Materials

SYSTEMS: Low-Cost (Li-Ion) Battery and Li-Polymer Battery

BARRIER: Cost limitations of Li-ion and Li-polymer batteries

OBJECTIVES: To develop low-cost manganese-oxide cathodes to replace vanadium oxide electrodes in Li-polymer cells and cobalt/nickel electrodes in Li-ion cells.

APPROACH: Our approach is to search for, characterize, and develop low-cost manganese oxide electrodes that can be used in Li-ion and Li-polymer cells; the electrodes will be synthesized in the discharged and charged states, respectively. For Li-ion cells, focus will be placed on layered lithium-manganese oxide structures that do not convert to spinel upon electrochemical cycling, particularly those derived from Li_2MnO_3 ; for Li-polymer cells, the material of choice is stabilized $\alpha\text{-MnO}_2$. (Note: At this stage of the project, we have downgraded the research priority to search for an alternative vanadium oxide electrode, such as V_6O_{13} , to replace the current material of choice, LiV_3O_8 , because in the Li-V-O system, LiV_3O_8 is still believed to be the best vanadium oxide electrode available for Li-polymer cells.)

STATUS OCT. 1, 2000: We have exploited the concept of using a Li_2MnO_3 component to stabilize layered LiMO_2 structures with the ultimate objective of stabilizing layered LiMnO_2 . In particular, we expanded our synthesis efforts to include solid solutions of $[\text{x}(\text{Li}_2\text{MnO}_3)\bullet\text{y}(\text{LiMO}_2)]$ compositions, where M = Mn, Ni or Co, or a combination thereof. Optimized compositions have yielded specific capacities of ~ 150 mAh/g between 4.5 and 3.0 V in Li half-cells at 50°C , but for less than 100 cycles.

EXPECTED STATUS SEPT. 30, 2001: Improvements in the electrochemical performance of $[\text{x}(\text{Li}_2\text{MnO}_3)\bullet\text{y}(\text{LiMO}_2)]$ electrodes will have been achieved. A performance target of 150 mAh/g for 100 cycles at 50°C in Li/ $[\text{x}(\text{Li}_2\text{MnO}_3)\bullet\text{y}(\text{LiMO}_2)]$ cells has been set. A more detailed understanding of the behavior of $[\text{x}(\text{Li}_2\text{MnO}_3)\bullet\text{y}(\text{LiMO}_2)]$ electrodes will have been gathered. Work on stabilized $\alpha\text{-MnO}_2$ electrodes for Li-polymer cells will have been initiated in collaboration with LBNL (J. Kerr) with an initial target reversible capacity set at 200 mAh/g for 50 cycles.

RELEVANT USABC GOALS: 10-year life, $<20\%$ fade over a 10-year period.

MILESTONES: The initial milestone (#1) to be reached by the end of April 2001 will be to achieve a reversible electrochemical capacity of 150 mAh/g from layered $[\text{x}(\text{Li}_2\text{MnO}_3)\bullet\text{y}(\text{LiMO}_2)]$ electrodes for 50 cycles at 50°C against a metallic Li counter electrode. This will be increased to 100 cycles by the end of September 2001 (#2). By then a more detailed understanding of the electrochemical and structural relationships of layered $[\text{x}(\text{Li}_2\text{MnO}_3)\bullet\text{y}(\text{LiMO}_2)]$ electrodes will also have been gathered.

PROGRESS TOWARD MILESTONES

- Accomplishments toward milestone 1 over last quarter**

Over the past quarter, we have continued to explore synthesis directions focused on stabilizing layered LiMO_2 structures with the aid of a Li_2MnO_3 ($\text{Li}[\text{Li}_{0.33}\text{Mn}_{0.67}]\text{O}_2$) component. Modified compositions utilizing other Li transition metal oxides with a rock salt component have been synthesized and cells built. A specific capacity above 150 mAh/g for some of these materials at 50°C has been achieved, but long-term cycling is compromised by capacity fade. A strategy has been developed to improve the cycling stability of these types of materials. In this respect, the distribution and arrangement of the Li and transition metal (M) ions in the layered structure is believed to be of critical importance to suppress the transition of layered LiMnO_2 structures to spinel. The phase diagram containing layered LiMnO_2 , MnO_2 and Li_2MnO_3 structures at the apices of a tie-triangle has been constructed (Fig. 1). Layered structures of composition $\text{Li}_{2-x}\text{MnO}_{3-x/2}$ ($0 < x < 2$) are formed by acid treatment of Li_2MnO_3 along tie-line A. One composition that has been isolated along this tie-line is $\text{Li}_{0.106}\text{MnO}_{2.053}$, alternatively, $\text{Li}_{0.103}\text{Mn}_{0.974}\text{O}_2$ that can be lithiated electrochemically along line B to the rock salt composition $\text{Li}_{1.026}\text{Mn}_{0.974}\text{O}_2$ ($\text{Li}[\text{Li}_{0.026}\text{Mn}_{0.974}]\text{O}_2$), which is close to that of the pure layered compound LiMnO_2 . The acid-leaching process leaves the manganese ions in octahedral coordination in a layered arrangement and in an ABBABBA stacking sequence to provide trigonal prismatic coordination for the remaining Li in the original Li-rich layer, *i.e.*, it has a P2-type structure. Subsequent electrochemical lithiation of $\text{Li}_{0.103}\text{Mn}_{0.974}\text{O}_2$ in a Li cell, which follows line B in Fig. 1, regenerates the cubic-close-packed arrangement of the oxygen array but maintains the layered configuration of the Mn ions. This configuration of the electrode structure appears to be retained upon subsequent delithiation and relithiation of the electrode. The theoretical capacity of the $\text{Li}_{0.103}\text{Mn}_{0.974}\text{O}_2$ electrode is 267 mAh/g, based on the mass of the fully discharged electrode; in practice, a rechargeable capacity of 150–170 mAh/g has been achieved at room temperature. We are attempting new synthesis routes to optimize the composition, structure and performance of these electrodes.

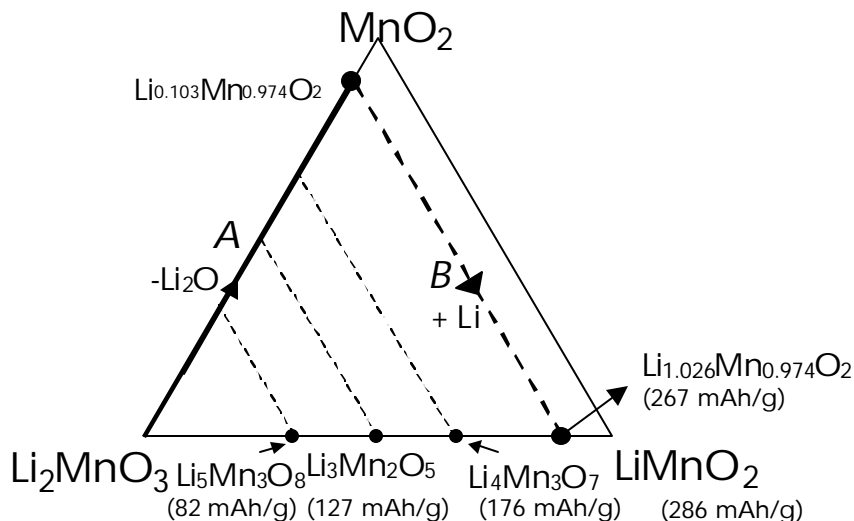


Figure 1. A schematic of the MnO_2 - Li_2MnO_3 - LiMnO_2 phase diagram.

- Further plans to meet or exceed milestones:** None
- Reason for changes from original milestones:** N/A

TASK STATUS REPORT

PI, INSTITUTION: M.S. Whittingham, SUNY at Binghamton

TASK TITLE - PROJECT: Cathodes – Novel Materials

SYSTEMS: Li/Polymer/Gel and Low-Cost Li-Ion

BARRIER: Lower-cost, higher-capacity and safer cathodes

OBJECTIVES: The primary objective is to find lower-cost and higher-capacity cathodes, exceeding 200 Ah/kg, that are based on benign materials.

APPROACH: Our cathode approach is to place emphasis on manganese dioxides, both pure and modified with other transition metals, using predominantly low-temperature synthesis approaches. These materials will be synthesized, and characterized both structurally and for thermal and chemical stability. All will be evaluated electrochemically in a variety of cell configurations.

STATUS OCT. 1, 2000: We determined that layered manganese dioxides can be structurally stabilized, that their stability is a function of current density and/or cut-off voltages, that their electronic conductivity can be significantly enhanced, that their cell cycling can be substantially improved by addition of other transition metals, and that hydrothermally synthesized manganese oxides cycle as well as high-temperature materials. We also showed that vanadium oxides can be stabilized by the addition of manganese ions

EXPECTED STATUS SEPT. 30, 2001: For low-cost Li-Ion cells, we expect to identify the changes in LiMnO_2 structure as a function of current density in cell cycling, to determine the structure and composition of the vanadium-stabilized LiMnO_2 and to increase its electrochemical capacity, to understand better the behavior of the $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Cr}_{0.4}\text{O}_2$ cathode and to determine if there is an iron analog. For Li/polymer cells we expect to complete the evaluation of the manganese-stabilized δ -vanadium oxides and to compare them to the iron phosphates. Emphasis in all cases will be placed on understanding the reasons for capacity fade.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestones this year are:

1. to characterize the pillared manganese oxide, and improve its capacity to 150 mAh/g with an ultimate goal of 200 Ah/kg.
2. to complete the characterization of manganese-stabilized vanadium oxides and to compare the best samples with iron phosphates for polymer or gel batteries by July 2001.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 over last quarter**

We are exploring the formation of larger quantities of this material.

- **Further plans to meet or exceed milestones:** None
- **Reason for changes from original milestones:** N/A

- **Accomplishments toward milestone 2 over last quarter**

We have explored the extension of our hydrothermal studies to the possible formation of lithium iron phosphate under mild conditions as a low-cost manufacturing process. The iron phosphate so formed would then be used as a comparison standard for our new cathode program. The iron phosphate was recently reported to have a higher rate capability than LiCoO_2 when appropriately carbon coated (Armand IBA 2001). It is therefore a particularly attractive cathode for large-scale Li batteries.

We have successfully formed pure LiFePO_4 at under 170°C in less than three hours of reaction time. The X-ray diffraction of the material formed is shown in Fig. 1, and is quite crystalline. SEM shows the particle size to be of the order of a μm . It cycles about 0.5 Li per formula unit in a regularly constructed cathode. Our next step is to carbon coat the material following the procedure in EP1049182A2 to increase the particulate conductivity. We will also explore microwave-assisted hydrothermal synthesis, which could reduce the reaction time to the order of minutes thus making a continuous reaction process viable.

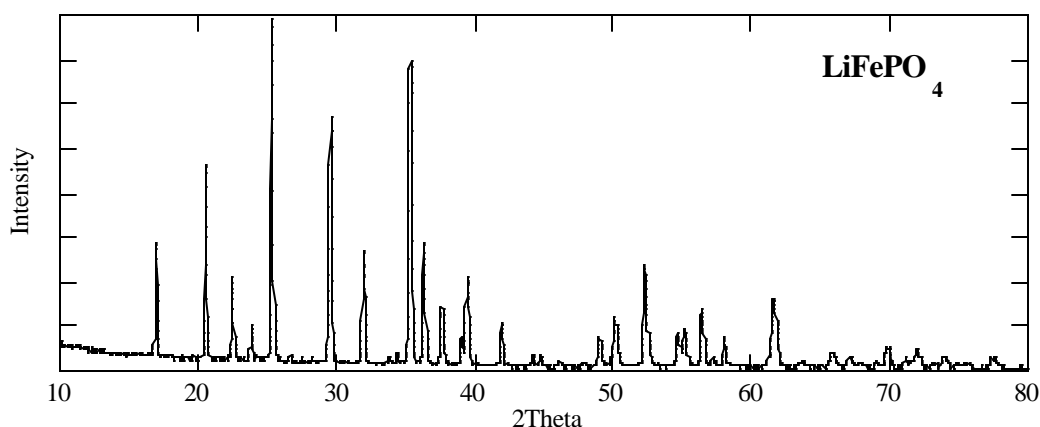


Figure 1. X-ray powder diffraction pattern of hydrothermally formed LiFePO_4 .

- **Further plans to meet or exceed milestones:** None
- **Reason for changes from original milestones:** N/A

Presentation

The Keynote lecture, "Insertion Electrodes: From Titanium Disulfide to Manganese Oxides and Manganese Vanadium Oxides," was given at the International Battery Association, Kwa Maritane, South Africa – March 2001.

TASK STATUS REPORT

PI, INSTITUTION: M. Doeff, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cathodes -Synthesis and Characterization of Cathode Materials for Rechargeable Lithium and Lithium Ion Batteries

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIERS: Cost, cycle life, safety, and energy density

OBJECTIVES: To develop low-cost cathodes based on benign materials (*e.g.*, manganese oxides, lithium iron phosphates) having electrochemical characteristics (*e.g.*, cycle life, energy and power densities) consistent with the goals of the USABC and/or PNGV.

APPROACH: Cathode materials are synthesized using both conventional solid-state techniques and solution methods (*e.g.*, sol-gel, glycine-nitrate combustion). The micro-structures and atomic structures of the materials are determined by relevant methods, and electrochemical analysis is carried out in a variety of cell configurations. Emphasis is placed on structurally stable materials such as tunnel-containing manganese oxides, as well as those of commercial interest, such as spinels and lithium iron phosphate.

STATUS OCT. 1, 2000: A tunnel-containing manganese oxide has been cycled more than 700 times in a Li/liquid electrolyte cell configuration, with little capacity loss and no structural change. Cells can be discharged repeatedly at up to 5 C rate with no damage. The effect of Ti-substitution upon the electrochemical characteristics has been determined, and a correlation between unit cell size and capacity has been observed.

EXPECTED STATUS SEPT. 30, 2001: The program will be expanded to include lithium iron phosphates and substituted spinels as required by the BATT program. We expect to have prepared samples of LiFePO_4 available for the program and to have made a preliminary determination of the electrochemical characteristics. We also will have determined if anion substitution of tunnel-containing manganese oxides is a viable approach to improving capacity.

RELEVANT USABC GOALS: 10-year life, < 20% capacity fade over a 10-year period.

MILESTONES: Our major milestone this year is to provide small samples (30 g) of conventional LiFePO_4 to the BATT program by early 2001. We are slightly delayed because of a furnace problem, which should be fixed shortly. As a substitute until we can provide the LiFePO_4 , we have delivered a sample of Li_xMnO_2 for use in baseline cells.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

We have succeeded in making a nearly phase-pure tunnel compound of approximate composition $\text{Na}_{0.42}\text{Cu}_{0.11}\text{Mn}_{0.89}\text{O}_2$ by glycine-nitrate combustion, and have delivered samples of Li_xMnO_2 with the $\text{Na}_{0.44}\text{MnO}_2$ structure to the Newman group for thermodynamic studies and to Dr. K. Striebel for baseline cells. We attempted to substitute 5.5% of the oxygen anions with fluorine in tunnel- MnO_2 by incorporating NaF or MnF_3 in the precursor mix prior to firing. XRD patterns of the products are somewhat ambiguous and there appears to be more than one phase present. Reaction conditions (*e.g.*, oxygen partial pressure) may need to be modified to obtain a phase-pure product.

Dr. Karim Zaghib of HydroQuébec supplied samples of carbon-coated LiFePO_4 for electrochemical characterization. This material shows superior performance to that of uncoated LiFePO_4 . We have assembled and discharged Li-polymer cells containing the HydroQuébec material. The cells exhibit a flat discharge profile at about 3.4 V and deliver 154 mAh/g (91% of theoretical capacity) at C/5 rate (Fig. 1).

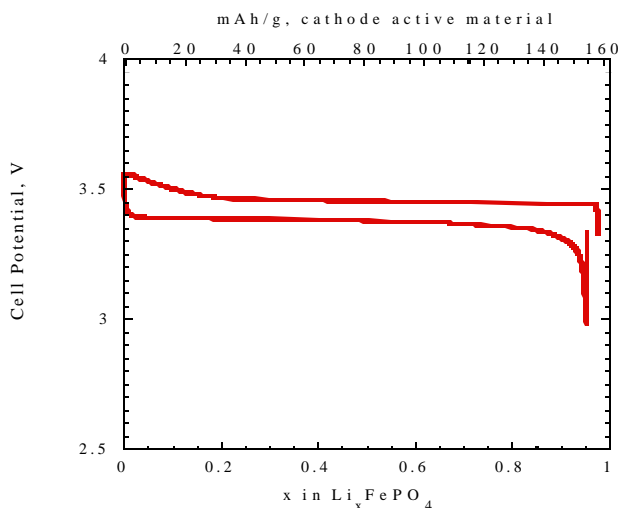


Figure 1. Second charge ($50 \mu\text{A}/\text{cm}^2$, top trace) and discharge ($0.1 \text{ mA}/\text{cm}^2$ or C/5 rate, bottom trace) of a Li/P(EO)₈LiTFSI/HQ- LiFePO_4 cell at 85°C . The positive electrode material is carbon-coated.

Publication

M.M. Doeff, A. Anapolsky, L. Edman, T.J. Richardson and L.C. De Jonghe, “A High-Rate Manganese Oxide for Rechargeable Lithium Battery Applications,” *J. Electrochem. Soc.* **148**, A230 (2001).

- **Further plans to meet or exceed milestones:** Modification of a furnace is underway for synthesis of pure LiFePO_4 .

- **Reason for changes from original milestones:** Our original goal to provide a small quantity of LiFePO_4 to K. Striebel for the building of baseline cells is delayed because of furnace problems. The furnace should be repaired shortly, and we should be able to deliver samples before the end of the fiscal year. We have provided a sample of Li_xMnO_2 for the baseline cell program instead.

BATT TASK 5 DIAGNOSTICS

TASK STATUS REPORT

PI, INSTITUTION: F. McLarnon, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics - Electrode Surface Layers

SYSTEMS: Li/Polymer and Low-Cost Li-Ion

BARRIER: Short lithium battery lifetimes

OBJECTIVES: The primary objective is to establish direct correlations between electrode surface changes, interfacial phenomena, and cell capacity decline.

APPROACH: Our approach is to use ellipsometry, Raman spectroscopy, and advanced microscopic techniques to characterize electrodes taken from baseline BATT Program cells, as well as thin-film electrodes in model cells. Data to be collected include changes in electrode surface morphology, electrode surface chemistry, and SEI thickness and composition, which accompany cell cycling.

STATUS OCT. 1, 2000: We defined the relationships between electrode history, electrolyte composition, electrode surface properties, and temperature for a model thin-film spinel LiMn_2O_4 cathode.

EXPECTED STATUS SEPT. 30, 2001: We expect to identify changes in $\text{LiAl}_{0.05}\text{Ni}_{0.80}\text{Co}_{0.15}\text{O}_2$ and $\text{Li}_{1.02}\text{Al}_{0.25}\text{Mn}_{1.75}\text{O}_{3.92}\text{S}_{0.03}$ cathode surface morphology and chemistry which accompany cycling in LiPF_6 -EC-EMC, LiTFSI +cross-linked PEO, and LiBF_4 + cross-linked gel electrolytes, and identify or confirm specific degradation modes. We expect to characterize SEI formation and growth on Li and carbonaceous anodes in LiPF_6 -EC-EMC, LiTFSI +cross-linked PEO, and LiBF_4 + cross-linked gel electrolytes, and determine the role of SEI growth in cell capacity and power loss.

RELEVANT USABC GOALS: 0 year life, < 20% capacity fade over a 10-year period.

MILESTONES: Our major milestone to determine the effect of sulfur additives on the surface chemistry of LiMn_2O_4 electrodes is expected to be completed by the planned date of April 2001, or shortly thereafter.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter:** We used Raman microscopy and Atomic Force Microscopy (AFM) to characterize cathodes from three Doo Youn cells: (i) a fresh cell discharged to 3.0 V, (ii) a fresh cell charged to 4.2 V, and (iii) a cell which was cycled 350 times at 0°C and then discharged to 3.0 V at the C/3 rate. Figure 1 shows Raman spectra of these cathodes. The peaks at 484 and 595 cm^{-1} in the spectrum of the discharged cathode are characteristic for the E_g and A_{1g} modes, respectively, of the hexagonal structure of LiCoO_2 , and the spectrum of the charged cathode shows two intense peaks at 467 and 665 cm^{-1} . The spectral changes correlate with known structural changes of LiCoO_2 , *i.e.*, a series of phase transitions to other hexagonal phases as well as monoclinic phases. Surprisingly, the spectrum of the cycled cell showed characteristics typical of a charged cathode, rather than a discharged cathode. The peak at 665 cm^{-1} remains very pronounced, and the E_g and A_{1g} peaks at 474 and 588 cm^{-1} are shifted toward lower frequencies, which is typical for delithiated hexagonal $\text{Li}_{1-x}\text{CoO}_2$. This indicates that active material at the electrode surface was not fully discharged, even though the cell potential was 3.0 V. Loss of cathode electronic conductivity, LiCoO_2 grain isolation, and electrode polarization followed by relaxation may explain this phenomenon, which probably contributes to the measured 10% capacity loss after 350 cycles. AFM images (Fig. 2) of the LiCoO_2 cathodes revealed similar electrode morphologies with no visible changes caused by cycling. The electrode surface consists of tightly packed 1-15 μm grains of LiCoO_2 . The grain top surfaces are flattened due to apparent mechanical calendaring during electrode manufacturing.

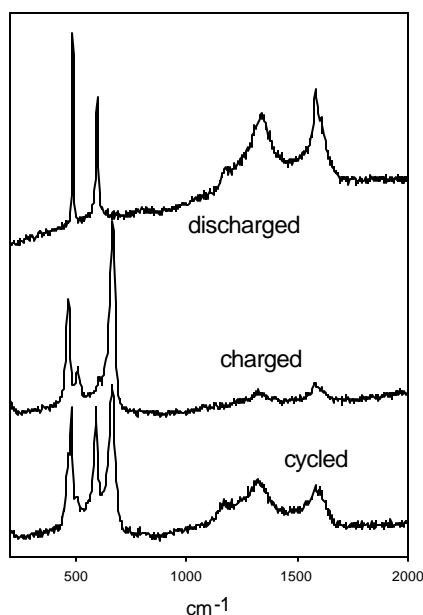


Figure 1: Raman spectra of cathodes from Doo Youn cells.

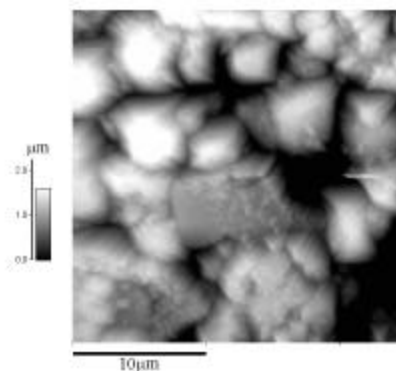


Figure 2: Typical AFM image of cathode from a Doo Youn cell.

- **Further plans to meet or exceed milestones:** We prepared a series of thin-film LiMn_2O_4 electrodes and characterized them by X-ray diffraction, as well as IR and Raman spectroscopy. The ~1 μm thick electrodes show spectral characteristics typical for a LiMn_2O_4 spinel. We are developing a sulfur-doping method to produce a thin and uniform sulfur coating. Sulfur deposition from its solution in CS_2 proved unsuccessful, and we are considering different approaches to this problem.

- **Reason for changes from original milestones:** N/A

TASK STATUS REPORT

PI, INSTITUTION: J. McBreen Brookhaven National Laboratory

TASK TITLE - PROJECT: Diagnostics - Structure and Characterization of Materials

SYSTEMS: Low-Cost Li-Ion

BARRIER: Short lithium battery lifetimes

OBJECTIVES: The primary objective is to establish direct correlations between electrode materials changes, interfacial phenomena, and cell capacity decline.

APPROACH: Our approach is to use a combination of *in situ* and *ex situ* synchrotron techniques to characterize electrode materials and electrodes taken from baseline BATT Program cells. Techniques that are sensitive to both bulk and surface processes will be used. This will include both K and L-edge X-ray absorption spectroscopy and transmission electron microscopy (TEM).

STATUS OCT. 1, 2000: We have completed an extensive study of the effect of Li and O stoichiometry on the phase behavior of spinel LiMn_2O_4 cathodes during cycling at ambient and at low temperatures. The effects of electrode history on the phase behavior of LiMn_2O_4 cathodes were also investigated.

EXPECTED STATUS SEPT. 30, 2001: We expect to identify the changes in $\text{LiNi}_k\text{Mn}_{2-x}\text{O}_2$ and $\text{Li}_{1.02}\text{Al}_{0.25}\text{Mn}_{1.75}\text{O}_{3.92}\text{S}_{0.03}$ when cycled in LiPF_6 -EC-DMC electrolyte. We also expect to develop a combination of electron yield and fluorescent XAS at transition metal K- and L-edges as a tool for identification of inorganic surface degradation products in cathodes.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES:

1. Completion of XAS studies of LiCrMnO_2 by April 2001.
2. Completion of XRD and XAS studies of $\text{LiNi}_k\text{Mn}_{2-x}\text{O}_4$ by June 2001.
3. Develop a combination of electron yield and fluorescent XAS at transition metal K- and L-edges as a tool for identification of inorganic surface degradation products in cathodes by September 30, 2001.
4. Determine electrolyte effect on stability of LiMn_2O_4 at elevated temperatures by December 30, 2001.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 over last quarter:** A paper on the XAS work on LiCrMnO_2 was prepared for publication, and was sent to our collaborators at NRC, Canada for their input.
 - **Further plans to meet or exceed milestone:** None.
 - **Reason for changes from original milestone:** N/A
-
- **Accomplishments toward milestone 2 over last quarter:** Further XRD work was done on three $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ materials ($x = 0.1, 0.3$ and 0.5) that were prepared by a sol gel process. $\text{LiNi}_{0.3}\text{Mn}_{1.7}\text{O}_4$ was charged to 5.1 V and was discharged to 1.2 V. There were voltage plateaus at 4.5, 4.0, 2.8 and 1.5 V. The XRD patterns on the 1.5 V plateau were very complex and indicate the formation of at least two new cubic phases.
 - **Further plans to meet or exceed milestone:** None.
 - **Reason for changes from original milestone:** N/A
-
- **Accomplishments toward milestone 3 over last quarter:** XAS measurements in both the electron yield and fluorescent mode were done at the K-edge of O and at the L-edges of the transition metal in several Li-ion cathode materials. Typical results for O K-edge are shown in Fig. 1. In the fluorescence measurements the sampling depth is about 1000\AA , whereas it is only 50\AA in the electron yield measurements. The results indicate that the metal-oxygen bonding is different in LiNiO_2 and LiCoO_2 . In LiCoO_2 the metal-oxygen bonding is the same in the bulk and on the surface of the material. In Ni based materials there are differences in the metal-oxygen bonding between the surface and the bulk.

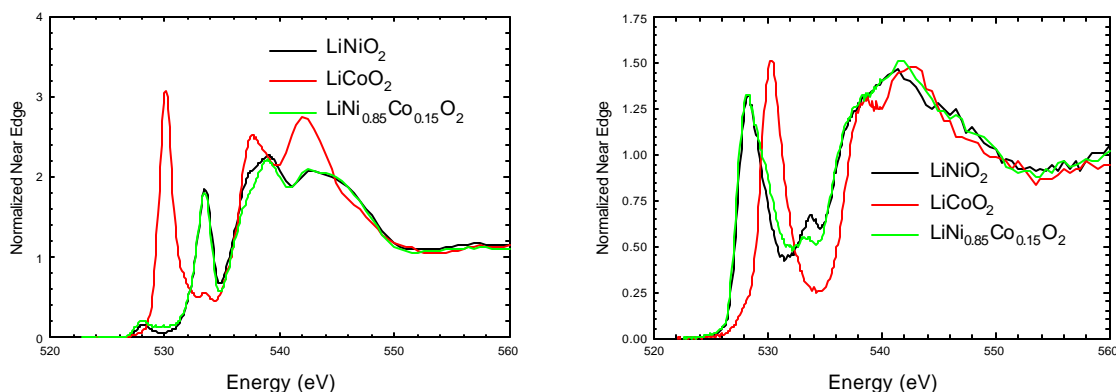


Figure 1. O K-edge (1s) spectra taken in electron yield mode (left) compared with those taken in fluorescence mode (right). Note the clear difference in the shape of the spectra of the Ni-based oxides due to the different sampling depths of the two techniques.

- **Further plans to meet or exceed milestone:** None.
 - **Reason for changes from original milestone:** N/A
-
- **Accomplishments toward milestone 4 over last quarter:** Work has begun on stability tests on LiMn_2O_4 when cycled at 55EC in coin cells with various electrolytes, including LiF based electrolytes.
 - **Further plans to meet or exceed milestone:** None.
 - **Reason for changes from original milestone:** N/A

TASK STATUS REPORT

PI, INSTITUTION: P.N. Ross, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics – Interfacial and Reactivity Studies

SYSTEMS: Low-Cost Li-Ion

BARRIER: Short lithium battery lifetimes

OBJECTIVES: The primary objective is to establish direct correlations between electrode surface changes, interfacial phenomena, and cell failure.

APPROACH: Our approach is to use Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) to study model electrode/electrolyte combinations, *e.g.*, using glassy carbon electrodes and BATT Program electrolytes, to provide the basis to interpret more-complex spectra recorded for ATD Program cell materials.

STATUS OCT. 1, 2000: We identified one of the mechanisms of SEI layer formation on carbon anode in EC-based electrolytes.

EXPECTED STATUS SEPT. 30, 2001: Establish thermal stability of the SEI layer on graphite anodes in GEN 2 electrolyte. Identify some routes to improved stability *via* electrolyte additives and/or graphite pre-treatment.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestone to install and calibrate a new IR microscope is postponed to April 2001 due to the delay of equipment funds. Another new milestone is set to demonstrate that one of our diagnostic techniques can identify a failure mechanism in a Li-ion battery.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 during last quarter:**

The microscope is being set up. It was demonstrated that the rotating ring disk electrode is useful in detecting reduction species, which helps in identifying SEI layer formation mechanism.

Figure 1 shows both of the disk and ring current profile when the disk electrode was scanned from 2 to 0.5 V, holding the ring electrode at 3.5 V in a 3% EC/THF – LiClO₄ electrolyte. The speed of rotation is 2000 rpm. The ring anodic current indicates that some soluble species from the EC reduction diffuses to the ring and is re-oxidized. The ring current becomes noticeable at potentials above 1 V (disk potential) and reaches a maximum when the disk potential drops to 0.5 V. The oxidation current collected at the ring is approx. 5% of the reduction current at the disk. In other experiments the disk potential was held at 0.5 V and the ring potential was scanned from 3.5 to 2.5 V. The results demonstrate that the reduced species are re-oxidized only above 3 V. The large potential difference between the reduction and re-oxidation, C.A. 2 V, suggests that solvent decomposition occurs during the reduction process, i.e the species being oxidized are fragments from the reduction reaction.

- **Further plans to meet or exceed milestone:**

XPS and AFM will complement the FTIR results in identifying a failure mechanism in Li-ion battery.

- **Reason for changes from original milestone:** N/A

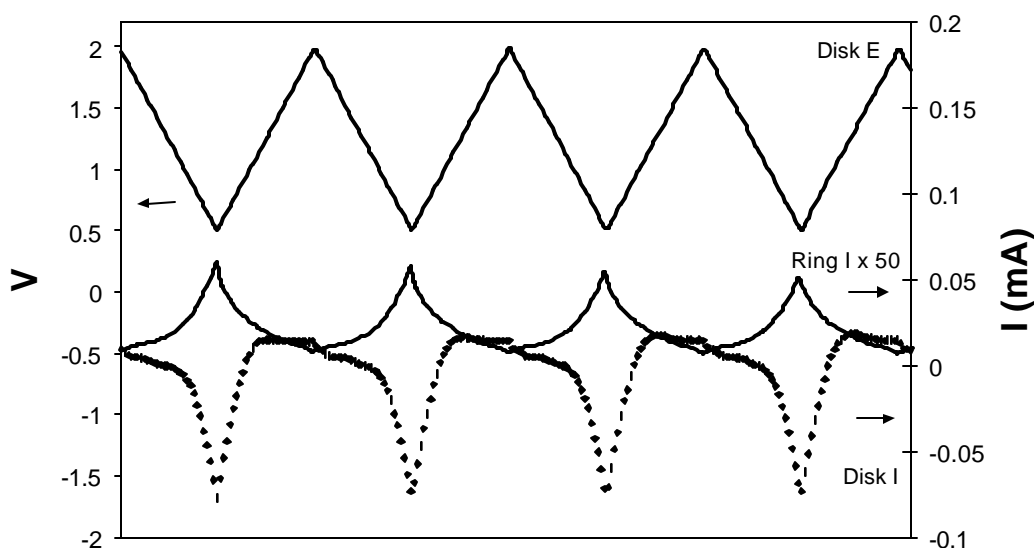


Figure 1.

TASK STATUS REPORT

PI, INSTITUTION: E.J. Cairns, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics - Synthesis and Characterization of Electrodes

SYSTEMS: Li-Ion and Li-polymer Batteries

BARRIER: Rapid capacity fade

OBJECTIVES: The primary objectives are (1) to directly observe Li in BATT Program cathode materials, characterize the Li atomic and electronic local environment, and determine changes in this environment with cycling; and (2) to synthesize intermetallics that have higher capacities than carbon electrodes and that demonstrate stable capacities during cycling.

APPROACH: Our approach is to use ^7Li MAS-NMR to characterize electrodes before and after cycling. Data to be collected are isotropic chemical shift, linewidth, and relaxation times for each species of Li. We prepare intermetallics in the Mg-Sn system by mechanical alloying. Characterizations are performed with X-ray diffraction and microscopy techniques.

STATUS, OCT. 1, 2000: Milling conditions to synthesize cubic and rhombohedral forms of Mg_2Sn were determined. Amorphous Mg-Sn alloys could not be produced by mechanical alloying in a typical high-power ball-mill. Attempts to synthesize a metastable, cubic $\text{Mg}_{5.67}\text{Sn}$ alloy were started. Cycling tests showed that cubic- Mg_2Sn capacities can exceed capacities for carbon electrodes, but the capacities fade below 100 mAh/g after a few cycles. Comparisons between fine-grained Mg_2Sn and coarse-grained Mg_2Sn show that the microstructure of these intermetallics influences electrochemical performance. X-ray diffraction of cycled electrodes indicates that a major mechanism for the capacity decay is conversion of the intermetallic into Mg and Sn.

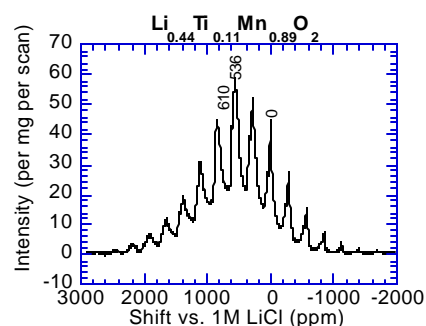
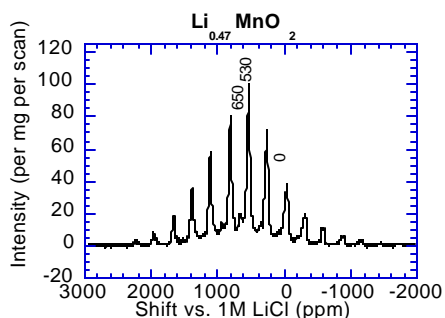
EXPECTED STATUS SEPT. 31, 2001: We expect to have concluded our evaluation of the Mg-Sn system. We plan to perform nuclear magnetic resonance experiments to aid in the characterization of the microstructure of the intermetallics and to determine sites that are occupied by Li. We expect to have identified the role of the microstructure in Mg_2Sn , studied through experiments on as-milled samples and on annealed samples, on the electrode capacity and cycle life. Similar work will be performed on the metastable, rhombohedral- Mg_2Sn phase to determine if this more conductive phase retains its structure during cycling.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestones are to compare NMR-observable properties of stoichiometric and substituted tunnel-structure electrodes before and after cycling, and to complete work on the cubic- Mg_2Sn phase by April 2001.

PROGRESS TOWARDS MILESTONES

- Accomplishments toward milestone 1 during last quarter:** ^7Li MAS NMR spectra for $\text{Li}_x\text{Ti}_y\text{Mn}_{1-y}\text{O}_4$ have been collected at two magnetic fields, allowing determination of the isotropic peaks. The spectra obtained at low field show much improved resolution over the previous results at high field. The linewidth for all peaks was nearly identical at both fields, indicating that chemical shift dispersion is the dominant contributor to linebroadening in these materials. The practical implication of this is that the highest resolution spectra will be obtained at the lowest field that will allow signal to be obtained in a reasonable time. The spectra show a small peak at 0 ppm and two larger peaks at higher shift. The peak at 0 ppm likely arises from Li-containing surface species. Both the unsubstituted and Ti-substituted materials show a peak near 530 ppm. This shift is very similar to that observed for Li in Li-Mn-O spinels, suggesting a similar local electronic structure. An additional peak is observed at 650 ppm in the unsubstituted material and 610 ppm in the Ti-substituted material. The shift of this peak is sensitive to average bulk manganese oxidation state, suggesting that the peak arises from Li in the vicinity of the substituent, as substitution is expected to affect the local manganese oxidation state to a greater extent than the bulk average oxidation state.



- Further plans to meet or exceed milestone:** The improved NMR spectrum resolution at low field should permit us to obtain relaxation times and linewidths for each isotropic peak. The relaxation times will allow the determination of a quantitative relationship between Li content and Li NMR signal intensity.
- Reason for changes from original milestone:** N/A
- Accomplishments toward milestone 2 during last quarter:** In connection with the work on anode materials, a differential capacity data and cycling data for Mg_2Si have been gathered for a variety of potential ranges. Raising the cutoff potential for Li insertion significantly reduces the discharge capacity, but improves the cycle life. The electrode cycled over 100-650 mV required 11 cycles to reach its maximum capacity. Very little capacity could be obtained after 20 cycles over higher cutoff potential windows (175-650 mV and 240-650 mV). Maximum capacities could be increased significantly by holding the potential at the cathodic limits after the limit was reached galvanostatically. When held for 24 hr for each cycle at the cathodic limit, maximum capacities of 430 mAh/g and 290 mAh/g were obtained for cycling over 100-650 mV and 175-650 mV, respectively. X-ray diffraction patterns for the electrodes with the higher cutoff limits show minimal structural degradation after cycling, *e.g.*, the Mg_2Si electrode cycled over 100-650 mV showed only small traces of Mg and no evidence of Si.
- Further plans to meet or exceed milestone:** We will attempt to use Sn NMR to quantitatively determine the amount of Sn in different environments in the Mg_2Sn intermetallics, particularly the amount of Sn in defect sites. This may help explain the differences in electrochemical performance between the samples with different microstructures.
- Reason for changes from original milestone:** N/A

TASK STATUS REPORT

PI, INSTITUTION: J. Evans, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics - EQCM Studies of the SEI on Carbon Anodes

SYSTEMS: High-power Li-ion battery

BARRIER: Irreversible capacity loss due to SEI formation and growth

OBJECTIVES: The primary objective is to understand SEI formation and growth on carbon anodes.

APPROACH: Our approach is to use an electrochemical quartz crystal microbalance (EQCM) to characterize the SEI formed on disordered carbon thin-film electrodes in model cells. Data to be collected are changes in mass of the SEI on the electrode and, thereby, the SEI growth with cell cycling is studied. A joint study to combine spectroscopic ellipsometry and EQCM gives us the SEI density.

STATUS OCT. 1, 2000: We estimated the SEI density on disordered carbon thin-film electrodes and observed mass changes corresponding to Li intercalation/deintercalation in 1M LiClO₄ / EC+DMC electrolyte.

EXPECTED STATUS SEPT. 30, 2001: We expect to correlate SEI formation and growth with the electrolyte LiPF₆ or LiTFSI / EC+DMC electrolyte and impurities (*e.g.*, H₂O).

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONE: Our major milestone to study the dynamic nature of the SEI as a function of electrolyte composition during cycling is expected to be completed by the planned date of July 2001.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

Cyclic voltammetry and EQCM were applied simultaneously to a carbon thin-film electrode in 1.2 M LiPF_6 / EC+DMC (20:80) electrolyte. Both cyclic voltammogram and EQCM data differ much from those for 1 M LiClO_4 / EC+DMC (50:50) electrolyte. First, cyclic voltammogram shows there are no substantial anodic currents flowing in the potential range between 3 V and 0 V vs. Li/Li^+ . This result coincides with the cyclic voltammogram for a HOPG thin-film electrode in 1 M LiPF_6 / EC+DMC (50:50) (refer to Fig. 1a and 1b of the “Electrode Surface Layers: Li-ion Batteries” Task Status Report in the October 1999 ETR Program Quarterly Report) in the sense that cathodic currents predominate in the same potential range. Considering the differences of carbon structure (disordered *vs.* graphite), Li salt molarity (1.2 M *vs.* 1 M) and solvent mixing proportion (20:80 *vs.* 50:50), the absence of anodic currents could be interpreted to be one of the electrochemical characteristics of carbon thin-film electrodes in LiPF_6 EC+DMC electrolyte. Therefore, the carbon thin-film electrodes might not be so attractive for negative electrodes with LiPF_6 -based electrolyte as carbon bulk electrodes, which are now adopted as negative electrodes in commercial Li-ion batteries. Galvanostatic cycling experiments also make clear the electrochemical difference of carbon thin-film electrodes in LiClO_4 and LiPF_6 -based electrolytes. The anodic capacity for LiClO_4 -based electrolyte increases from 50% of the cathodic capacity during the first cycle to almost 100% of the cathodic capacity during later cycles, which means that irreversible SEI formation does not occur. On the other hand, the anodic capacity for LiPF_6 -based electrolyte is negligible fraction of the cathodic one during every cycle.

The measured resonance frequency change for LiPF_6 -based electrolyte shows that something heavier (than the SEI that forms at carbon/ LiClO_4 -based electrolyte) accumulates on the carbon electrode throughout the cycles. The frequency change for LiClO_4 -based electrolyte during the first cycle is about 1000 Hz and that from the second to 20th cycle is about 400 Hz. This observation is not contrary to the current understanding that the SEI forms mostly during the first few cycles and this SEI acts as a passivating film, which prevents from continuous electrolyte decomposition. By contrast, the frequency changes for LiPF_6 -based electrolyte during both first and second cycles are all about 2000 Hz. The frequency keeps decreasing, which means mass increasing, until the detectable mass change reaches the instrument limit. It is known that the main SEI component in LiPF_6 -based electrolyte is LiF , the decomposition product of LiPF_6 . If we resort to this established opinion, the huge and monotonic frequency change could be attributed to the continuous LiPF_6 decomposition and, therefore, this decomposition product becomes so thick as to prevent Li-ions from penetrating through the film. The SEI for LiPF_6 -based electrolyte cannot act as an effective passivating film for carbon thin-film electrodes and this could be the reason why we could observe neither anodic current nor mass decrease.

- **Further plans to meet or exceed milestone**

Cyclic voltammetry, with the same experimental conditions, will be conducted for LiPF_6 /EC+DMC or LiTFSI/EC+DMC electrolytes. The same analysis for SEI formation and growth will be made and the results will be compared with our past results on LiClO_4 /EC+DMC.

- **Reason for changes from original milestone:** N/A

BATT TASK 6 MODELING

TASK STATUS REPORT

PI, INSTITUTION: J. Newman, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Modeling - Improved Electrochemical Models

SYSTEMS: Li/Polymer and Low-Cost Li-Ion

BARRIERS: Poor polymer transport properties, thermal management, dendrite formation

OBJECTIVES: Develop experimental and computational methods for measuring and predicting transport, kinetic, and thermodynamic properties. Model electrochemical systems to optimize performance, identify limiting factors, and mitigate failure mechanisms.

APPROACH: Use galvanostatic polarization technique to measure a complete set of transport properties, which aids selection of improved polymer electrolytes. Develop molecular dynamics program to predict diffusion coefficients in multicomponent solutions. Use potentiometric technique to measure entropy and develop thermal model that accounts for concentration effects in insertion electrodes, in order to improve thermal management. Develop model of factors affecting dendrite formation on Li metal. Use Raman spectroscopy to measure *in situ* concentration profile and dendrite growth.

STATUS OCT. 1, 2000: Measured transport properties in PEMO-LiTFSI polymer electrolyte and improved the measurement technique. Completed computer program and simulations for electrolyte diffusion coefficient of NaCl and KCl in water. Used calorimetry to validate energy balance. Measured entropy in manganese oxides. Developed a preliminary model for dendrite growth which includes effects of surface tension. Developing Raman spectroscopy methods to examine dendrite growth *in situ*.

EXPECTED STATUS SEPT. 30, 2001: We expect to complete measurements of the transport properties of PEMO-LiTFSI and to complete refinement of both the galvanostatic polarization method and the transition-time verification method. Modification of the molecular dynamics program to predict diffusion coefficients in multicomponent electrolytes currently of interest to the BATT program, such as LiBF₄ in EC:PC, will be ongoing. Measurements of the entropy of reaction in BATT baseline materials will be completed. Modeling of the SEI layer will be ongoing. Refinement of a model of dendrite growth to include relevant physical effects will be ongoing, as will experimental work to observe dendrite growth and concentration profiles *in situ* using confocal Raman spectroscopy.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, <20% capacity fade.

MILESTONES:

1. Preliminary model of transport through the SEI layer by August 1, 2001.
2. Design a cell container for *in situ* confocal Raman microscopy by July 1, 2001.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 during last quarter:**

Side reactions in the Li / LiTFSI-PEMO system are being characterized to determine their impact on measurement of transport properties. Progress was made in two areas: 1) (With John Kerr) Transition time measurements at several concentrations and 85°C indicate that the relative significance of side reaction(s) increases with decreasing salt concentration in PEMO-LiTFSI. Similar measurements in PEMO-lithium triflate show no evidence of side reaction; thus, we believe the side reaction in the LiTFSI electrolyte involves the TFSI anion. 2) A model is being developed to explore the effects of a side reaction on the behavior of a cell during galvanostatic or potentiostatic polarization.

Changes to the molecular dynamics computer code to permit simulation of multicomponent carbonate electrolytes are ongoing.

It is well known that alloy electrodes rapidly lose capacity upon cycling in organic electrolytes. However, excellent cycling has been achieved with alloy electrodes in molten salt electrolytes at high temperatures. Therefore, interactions with the electrolyte must be playing a crucial role in the interparticle contact. We have begun experiments on tin-lithium alloy electrodes in ether and in carbonate electrolytes to identify how interactions with the solvent affects capacity fade.

- **Further plans to meet or exceed milestone:** The focus of this modeling project will shift to modeling the effects of the SEI layer on interparticle contact.

Measurement of the entropy of reaction as a function of state of charge in tunnel LiMnO₂ is in progress.

- **Reason for changes from original milestone:** Result of literature review.

- **Accomplishments toward milestone 2 during last quarter**

(With Robert Kostecki) The measurements of transport properties can be verified independently by using *in situ* confocal Raman spectroscopy to measure concentration profiles during passage of current. Several designs have been tried to achieve a cell that is of well-defined geometry, air-tight, inert, transparent, and uniform temperature. Further improvements are still needed to insure uniform temperature and a well-defined geometry.

The previously developed model for dendrite growth has been used to evaluate the effect of salt diffusivity, separator thickness, and other variables on the rate of dendrite growth. Surface energy has been shown to have a lesser effect on dendrite growth than separator thickness or current density. The analysis of interfacial forces using elasticity theory shows that the properties of the separator control the dendrite growth rate as much or more than surface forces during the early stages of growth. *In situ* confocal Raman spectroscopy could elucidate the effect of electrolyte concentration profiles on dendrite growth. See above for the progress of these experiments.

- **Further plans to meet or exceed milestone:** None
- **Reason for changes from original milestone:** N/A

TASK STATUS REPORT

PI, INSTITUTION: A.M. Sastry, University of Michigan

TASK TITLE - PROJECT: Modeling - Failure Mechanisms in Li-ion Systems: Design of Materials for High Conductivity and Resistance to Delamination

SYSTEMS: Low-Cost Li-Ion

BARRIER: Short lithium battery lifetimes

OBJECTIVES: The primary objective of these studies is to explain and predict the role of conductive and mechanical failures on reduced performance in the baseline systems, by tightly coupled experimental and simulation studies of microscale transport and mechanics phenomena.

APPROACH: Correlation of delamination, high impedance and temperature/structure/function phenomena with specific materials composition and morphology will be developed, making use of the extensive software developed for tracking mechanical and conductive losses in heterogeneous materials at UM. Specific comparisons will be undertaken, using cells provided by the ATD and BATT programs.

STATUS OCT. 1, 2000: We developed finite element representations of model carbon materials, and developed a means for measuring conductivity of thin electrodes.

EXPECTED STATUS SEPT. 30, 2001: We expect to confirm structure/function relationships in ATD Gen 1 and Gen 2 cells, through image analysis and testing, with verification from finite element simulations.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: We expect to test DOE ATD Program Gen 1 and 2 cells, provided by Argonne National Laboratories, by May 31, 2001 (start date: 2/01).

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

We have completed conductivity testing and initiated image analysis of materials from three laboratories participating in DOE-sponsored efforts: Argonne National Laboratory (Dr. Gary Henriksen, contact), Lawrence Berkeley National Laboratory (Dr. K. Kinoshita, contact), and the Institut de Recherche d'Hydro-Québec (Dr. Karim Zaghib, contact). Anode (LBNL, IREQ) and cathode (ANL) materials have been tested.

We have further advanced simulations development, and are now at the stage where we can begin simulation of realistic particles' conductivities. We have separated the particles for study by aspect ratio, and have also now assembled key materials properties for constituent carbons. We have also further advanced our simulations capabilities in mechanics, including completing a series of simulations of fiber-fiber interconnects for arbitrary angles. Through these techniques, we will be able to advance our efforts in ellipsoidal and flake geometries in the next project months. Our main accomplishments thus far are:

1. experimental conductivity mapping of materials provided by three DOE-sponsored laboratories, using a four-probe conduction experiment.
2. conductivity code for automatic generation of irregular arrays of conductive particles, and code benchmarking against classical models, with recently added features to handle boundary effects and irregular particle connections
3. mechanics modeling of simple interconnects, allowing 3D results to be used to implement revised mechanics assumptions in faster, more efficient 2D simulations.

- **Further plans to meet or exceed milestone**

We have continued our collaborative efforts with ANL and LBNL in experimentation on cycled and uncycled electrodes. We have also begun a collaboration with IREQ. Our conduction and mechanics simulations have advanced in the project period. In conduction, we are now embarking on a series of comparative simulations between numerical predictions and carbon conductivities in anode materials.

- **Reason for changes from original milestone:** N/A

TASK STATUS REPORT

PI, INSTITUTION: J. Evans, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Modeling - Thermal Modeling of Li Batteries

SYSTEMS: Li-polymer (Li-ion)

BARRIER: Thermal management and safety issues, battery efficiency

OBJECTIVES: The objective is the ability to predict the thermal behavior (including stability) and efficiency of Li batteries for use in electric or hybrid vehicles.

APPROACH: The approach is a combination of mathematical modeling and experimental measurement. The modeling couples the numerical solution of the equations for heat generation and transport within a battery to the equations describing battery electrochemistry. The experiments are to measure fundamental properties for input into the model or for comparison with model predictions. Thermal conductivities of cell components are measured, as are heat generation rates, in laboratory and commercial cells.

STATUS OCT. 1, 2000: A coupled mathematical model had been developed and found to show a reasonable fit to limited experimental data on heat generation during discharge of laboratory Li-polymer cells.

EXPECTED STATUS SEPT. 30, 2001: Refinements of the mathematical model will be completed. The electrochemical calorimeter will be used to measure the heat generation rate of a limited number of commercial Li-ion batteries.

RELEVANT USABC GOALS: 75-80% discharge efficiency, thermal loss 15% of capacity in 48hrs, safety.

RELEVANT USABC GOALS: Tolerance to abusive operating conditions.

MILESTONES: Completion of measurements on Li-polymer cells available under the BATT program - September 2001

PROGRESS TOWARDS MILESTONES

Accomplishments towards milestones over last quarter

No progress has been made this quarter. The graduate student previously engaged in this project, Scott Beckman, left to work on another project (where funding was both sufficient and certain) at the end of last quarter. This was a fortunate choice, on his part, because there were insufficient funds to support him and the other graduate student (Kyungjung Kwon) working from BATT funds in Evans' group. With funding as it is at present, it would be irresponsible to seek a graduate student to replace Beckman.

Further plans to meet or exceed milestones:

The electrochemical calorimeter now appears to be working properly. An undergraduate, who assisted Scott Beckman in the Fall, will use the calorimeter to measure heat generation rates in BATT and commercial Li cells over the summer months.

Reasons for changes from original milestones: N/A

PROPOSALS UNDER REVIEW

ORGANIZATION (Principal Investigator)	TITLE	STATUS
Illinois Institute of Technology (J. Prakash)	Development of Nonflammable Electrolytes for Lithium-Ion Batteries	Renewal Proposal - Contract Placed
Northwestern University (D.F. Shriver)	Highly Conductive Polyelectrolyte-Containing Rigid Polymers for Lithium or Lithium-Ion Batteries	Renewal Proposal - Contract Placed
Covalent Associates (A.B. McEwen)	Non-Flammable Electrolytes for Lithium-Ion Batteries	Renewal Proposal - Rejected
North Carolina State Univ. (Khan, Fedkiw, Baker)	Composite Polymer Electrolytes for Use In Lithium and Lithium-Ion Batteries	Renewal Proposal - Contract Placed
HydroQuébec (K. Zaghib)	Research on Lithium-Ion Polymer Batteries Utilizing Low Cost Materials	Unsolicited Proposal - In Negotiation
University of Michigan (A.M. Sastry)	Failure Mechanisms in Li-Ion Systems: Design of Materials for High Conductivity and Resistance to Delamination	Renewal Proposal - Contract Placed
SUNY @ Binghamton (M.S. Whittingham)	Novel Anode Materials Novel Cathode Materials	Renewal Proposal - Under Review

BATTERIES FOR ADVANCED TRANSPORTATION TECHNOLOGIES (BATT)

QUARTERLY REPORT FOR JANUARY – MARCH 2001

CALENDAR OF UPCOMING EVENTS

January 2001

- 4 - 7 3rd Hawaii Battery Conference (HBC2001) - Kamuela, HI (Dr. A.N. Dey, ARAD Enterprises, 39 Poko Place, Hilo, HI 96720; tel/fax: (508) 759-4617; lithium@capecod.net) The Outrigger Waikoloa Beach Resort
- 9 - 12 16th Annual Battery Conference on Applications and Advances - Long Beach, CA (Hitesh Somani, Conference Coordinator, Das, Annual Battery Conference, Dept. of Electrical Engineering, Cal State Long Beach, 1250 Bellflower Blvd., Long Beach CA 90840-8303; (562) 985-4605; fax: (562) 985-7561; battery@csulb.edu)

March 2001

- 11 - 14 14th IBA Battery Materials Symposium - South Africa (Edward Coombs, +27 13 7593500; fax: +27 13 7526002; ecoombes@deltaemd.co.za; Mike Thackeray, (630) 252-9184; fax: (630) 252-4174; thackeray@cmt.anl.gov) Kwa-Maritane Game Lodge
- 25 - 30 199th Electrochemical Society Meeting – Washington D.C. (Mr. Brian E. Rounsavill, The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; brian@electrochem.org;
<http://www.electrochem.org/staff/brian/html>)

April 2001

- 2 - 5 Space Power Workshop – Redondo Beach, CA (Jackie Amazaki, 301-336-4073; Jacqueline.y.amazaki@aero.org; <http://www/aero.org/conferences/power>) Crowne Plaza
- 17 - 19 Batteries 2001 – Paris, France (www.batteries2001.com)

May 2001

- 11 - 14 PES 2001, Polymer Electrolytes Symposium – The Netherlands (Symposium Secretariat: c/o LGCE, P.O. Box 83005, NL-1080 AA, Amsterdam, The Netherlands; +31 20 679 3218; fax: +31 20 675 8236; PES2001@lgce.nl)

July 2001

- 1 - 6 International Conference on Materials for Advanced Technologies – ICMAT 2001 – Singapore (B.V.R. Chowdari, Department of Physics, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260; 65-874-2956; fax: 65-777-6126; phychowd@nus.edu.sg; <http://www/mrs.org.sg/icmat2001>)
- 9 - 13 International Conference on Electrified Interfaces: 9th in a Series on Non-Traditional Methods – Nova Scotia (Dr. Sharon G. Roscoe, Chemistry Dept., Acadia University, Wolfville, Nova Scotia, Canada B0P 1X0; fax: 1 9025851114; sharon.roscoe@acadiau.ca)

September 2001

- 2 - 7 200 ECS - Joint International Meeting of ISE and ECS– San Francisco CA (Dr. O. Dossenbach; odossenbach@pingnet.ch)

May 2002

- 12 - 17 201st Electrochemical Society Meeting – Philadelphia, PA – ECS Centennial Meeting (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org)

June 2002

- 23 – 28 11th International Conference on Lithium Batteries (IMLB-11) – Monterey CA (IMLB 11 Conference Secretariat, c/o The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; <http://www.electrochem.org/meetings/011/imlb11.html>)

September 2002

- 3 - 8 53rd ISE – Dusseldorf, Germany (Prof. J.W. Schultze, Institut für Physikalische Chemie II, Universität Dusseldorf, Universitätsstr 1, D-4000 Dusseldorf 1, Germany; fax: 49 2118112803; schultzj@rz.uni-duesseldorf.de)

October 2002

- 15 - 18 17th International Electric Vehicle Symposium & Exposition – Montreal, Canada (Ms. Pam Turner, EVS-17 Symposium Manager; (650) 365-2802; fax: (650) 365-2687; electricevent17@aol.com).
- 6 - 11 202nd Electrochemical Society Meeting – Salt Lake City, UT (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org)

August 2003

- 31 – Sept. 5 54th ISE – Florianopolis, Brazil (Prof. L.A. Avaca)

September 2004

- 55th ISE – Thessaloniki, Greece (Prof. E. Theodoridou)